THE EQUILIBRIUM BETWEEN CHROMIUM AND OXYGEN IN LIQUID IRON

THESIS

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I N D E X

INTRODUCTION

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Accurate knowledge of the equilibrium between chromium and oxygen dissolved in liquid iron is of great importance in the manufacture of alloy steels containing chromium. Despite the fact that a considerable amount of research work has been done on the processes controlling the production of alloy steels, still the discrepancies in the available data by the various investigators are so wide that the theory of alloy steel making cannot be placed on a sound theoretical basis.

Chromium is one of the main constituents in most alloy steels and the major alloying element in stainless steel. Since chromium forms carbides, a very low carbon content is desirable in the high chromium stainless steels to ensure high resistance to corrosion. The selective oxidation of carbon from high chromium melts has long presented a problem in that chromium is also oxidised. High temperatures are very desirable to minimise the loss of chromium to the slag. In order to assess the best conditions for decarburisation and for minimum oxidation of chromium and iron accurate data must be available on the effect of temperature on the Fe-Cr-C-O system.

There is a considerable scatter in the existing data on this system. In view of the importance in metallurgical processes of chromium and its oxides and Fe-Cr alloys, accurate data on this system would be a useful contribution towards the theory of alloy steel making. It would then be quite possible to extend this work to cover more complex alloy steels.

However, the foremost requirement is the basic thermodynamic data relating iron-chromium-oxygen alloys and this forms the basis of the present work. The thermodynamic properties of iron-chromium-oxygen alloys have been studied at 1700°C by equilibrating iron-chromium melts with hydrogen/water vapour mixture, a technique which has been employed with considerable success in previous gas-metal studies.

REVIEW OF LITERATURE

(1) IRON-OXYGEN SYSTEM

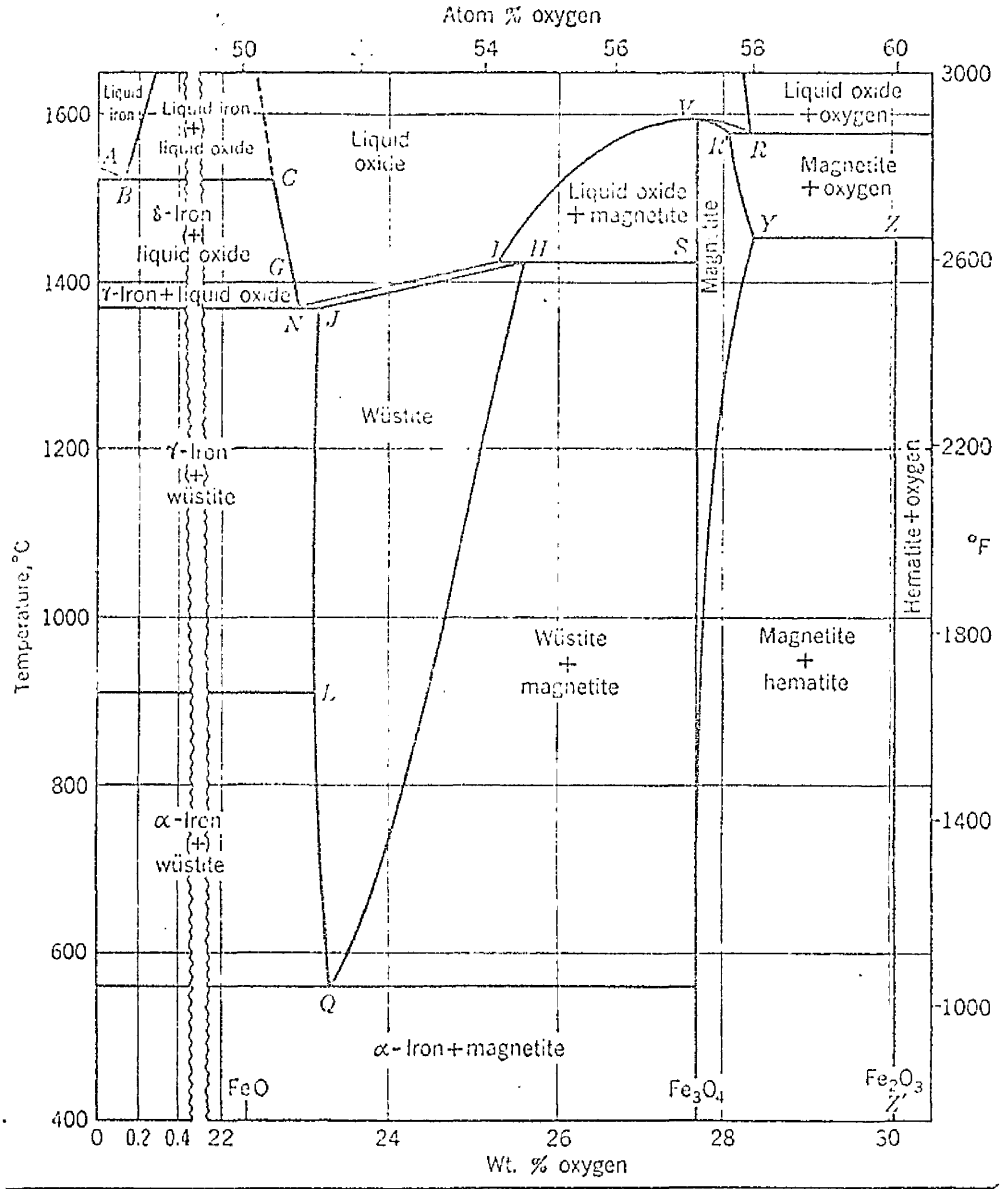
For a clear understanding of the basic reactions in steelmaking, it is important to know the thermodynamic proportion of oxygen in the molten steel. Oxygen dissolves in the liquid iron according to the equation:

$$O_2 \longrightarrow \underline{2O}$$

The symbols underlined represent dissolved elements in liquid iron.

It is usually found that liquid iron contains measurable amounts of oxygen. The solubility of oxygen in liquid iron increases with temperature. Different equations have been given for the oxygen solubility by various workers, these will be discussed later. Also it is found that the oxide in equilibrium with the metal is non-stoichiometric and the Fe/O ratio in the oxide increases with increasing temperature. It is probable that the immiscible metal and oxide phases become more miscible at higher temperatures and that ultimately the miscibility gap vanishes.

The equilibrium diagram for the Fe-O system by Darken and Gurry [1] is shown in Fig. (1). The solubility of oxygen in liquid iron is limited by the formation of a liquid iron oxide phase.



Point	°C	% O	p_{CO_2}/p_{CO}	Point	°C	% O	p_{CO_2}/p_{CO}	p_{O_2} (atm)
A.....	1539			*Q*.....	560	23.26	1.05	
B.....	1528	0.16	0.209	*R*.....	1583	28.30		1
C.....	1528	22.60	0.209	*R'*.....	1583	28.07		1
G.....	1400*	22.84	0.263	*S*.....	1424	27.64	16.2	
H.....	1424	25.60	16.2	*V*.....	1597	27.64		0.0575
I.....	1424	25.31	16.2	*Y*.....	1457	28.36		1
J.....	1371	23.16	0.282	*Z*.....	1457	30.04		1
L.....	911*	23.10	0.447	*Z'*.....		30.06		
N.....	1371	22.91	0.282					

FIG 1 THE IRON – OXYGEN PHASE DIAGRAM

The partial pressure of oxygen at which this phase appears has been found to be so low that it cannot be measured accurately by direct methods. Experimentally, to study the oxygen pressure in equilibrium with iron-oxygen solutions, a controlled mixture of other gases, commonly $H_2O - H_2$ or $CO_2 - CO$ is used. The most convenient experimental method to study the activity and free energy of oxygen in liquid iron is by means of the reaction as under:

$$H_2(g) + \underline{O} = H_2O(g) \quad \ldots\ldots\ldots\ldots (1)$$

$$K_1' = \frac{pH_2O}{pH_2 \times \underline{O}}$$

In view of the importance of the behaviour of oxygen dissolved in liquid steel as a refining agent, a number of researches have been carried out on the above reaction by various workers. Chipman [2] made one of the earliest studies on this reaction, by passing a controlled mixture of hydrogen and water vapour over a small charge of electrolytic iron, heated by induction. The charge was held in the molten condition at constant temperature for varying periods up to a maximum of 2 hours for the establishment of equilibrium. The metal was then allowed to solidify and its oxygen content determined by the vacuum fusion method. Chipman's[2] equilibrium data showed that the value of K_1' changes with oxygen concentration, thus indicating a deviation

of the system from the laws of ideal solution. The results in this work [2] were mainly confined to low oxygen concentrations and the few experiments at higher oxygen concentrations were rejected for the reason that liquid ferrous oxide was ejected from these melts during cooling and the analytical results were therefore, lower than the equilibrium oxygen concentrations.

Fontana and Chipman[3] extended this work to the limiting solubility of oxygen in liquid iron. Their experimental technique was basically the same as that used by Chipman[2], except that to avoid errors due to the thermal diffusion, the gaseous mixtures were preheated and secondly some of the melts were quenched in molten tin or water in an effort to retain the high temperature equilibrium oxygen concentration in the metal. Contrary to the previous data [2] it was found that the equilibrium constant of the reaction (1) was a true constant at all oxygen concentrations upto and including saturation and that the activity of oxygen was proportional to its concentration not only in dilute solutions but in all ranges of oxygen concentrations.

Samarin and Chipman[4] studied the effect of temperature on the reaction (1). The experimental procedure was exactly the same as that used by the previous workers[3]. They[4] confirmed the work of Fontana and Chipman[3].

Dastur and Chipman[5] in a later study of the reaction (1) stated that errors due to thermal diffusion could be eliminated by diluting the water vapour/hydrogen mixture with argon in the ratio of 1 : 4 and preheating the inlet gases upto the temperature of the melt. They also concluded from their limited study that K'_1 was constant.

Gokcen[6] studied the equilibrium in the reaction (1) and also the following reactions in the range of 1550° - 1700°C.

$$CO + \underline{O} \rightleftharpoons CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$K'_2 = \frac{pCO_2}{pCO \times \% \underline{O}}$$

$$H_2 + FeO \rightleftharpoons H_2O + Fe \quad \ldots\ldots\ldots\ldots (3)$$

$$K'_3 = \frac{pH_2O \cdot NFe}{pH_2 \cdot NFeO}$$

The solubility of oxygen in liquid iron was obtained from the data on reaction (1) and (3). Combination of the data on reaction (1) and the data on reaction (3) (and the corresponding reaction lead to)

$$FeO\ (l) = Fe(l) + \underline{O} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

$$K'_4 = \frac{\% \underline{O} \times NFe}{NFeO}$$

The equation given for the solubility of oxygen in liquid iron was as follows:

$$\log K_A = -\frac{5,762}{T} + 2,435$$

$$\text{or } \log \%\underline{O}\ (\text{maximum}) = -\frac{5,762}{T} + 2,435$$

which gave the solubility of oxygen in iron at its melting point (1530°C) as 0.17%.

Values of K_2' were also calculated by means of the known free energies of the gases involved in the water gas reaction. Reaction (1) and (2) are related by the well known water gas reaction.

$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

$$K_{wg} = \frac{pH_2O \times pCO}{pH_2 \times pCO_2} = \frac{K_1}{K_2}$$

Gocken[6] attributed the disagreement in the previous results to thermal diffusion and inaccurate oxygen analysis. He[6] used the technique of bubbling the gaseous mixture through the melt to eliminate thermal diffusion.

Floridis and Chipman[7] in their study of the reaction (1) found that the results obtained when a 6 : 1 argon to hydrogen ratio was used in the induction furnace and those obtained when the gaseous mixture was bubbled through the melt in a resistance furnace were in fair agreement. The equation

given by Floridis and Chipman[7] showing the effect of temperature on the equilibrium constant of reaction (1) was:

$$\log K_1 = \frac{7,050}{T} - 3.20$$

$$\Delta G^0 = -32,220 + 14.63\ T \text{ cals.}$$

At the time of the investigations (3,4,5) it was considered from the work of Tritton and Hanson [8], Herty and Gains[9] and Korber and Oelsen[10] that the solubility of oxygen in iron at 1530°C was about 0.21%. It was thought that upto this oxygen concentration there had been no primary wustite present before quenching the melts. Later data on the solubility of oxygen in iron at its melting point by Chipman and Fetters[11], Taylor and Chipman[12] and Gokcen[6] showed it to be 0.17% oxygen at 1530°C. The higher values of monotectic composition in the iron-oxygen system reported by the earlier workers [8,9,10] were probably due to inaccurate temperature measurements. The optical pyrometer under the experimental conditions might have given low temperature readings due to metallic film formation on the glass window, while the actual temperature might be higher, thus giving higher values of oxygen solubility.

The data of Fontana and Chipman[3] showed that K_1' was independent of oxygen concentrations upto about 0.21%. They[3] based their conclusions on the results of 6 experiments in

the range 0.16 - 0.22% oxygen for which the value of K_1' was in approximate agreement with those of heats containing less than 0.07% oxygen. The later knowledge of oxygen solubility in iron showed that the monotectic point lies at about 0.16% oxygen. It is therefore quite possible to believe that the group of experimental melts lying above 0.16 pct. oxygen might all have lost appreciable amounts of iron oxide during freezing, because the quenching technique used by these workers[3] induces freezing from the bottom upward. This loss of primary liquid wustite during slow solidification would have given low oxygen equilibrium concentration and thus a higher value of K_1'. The agreement with the results at lower oxygen concentrations may possibly be incidental. Unfortunately, no heats had been made in the range 0.07 - 0.1o pct. oxygen.

The work of Dastur and Chipman[5] was limited to oxygen contents below 0.06 pct. Although there was less liklihood of loss of oxygen during solidification, because the range studied was well below saturation, it still did not give enough proof that K_1' is constant upto the saturation value for oxygen in iron.

Reaction (1) was also studied by Matoba[13], Avorin, Polyakov and Samarin[14] and more recently by Sano and Sakao[15] In the work of Sano and Sakao[15] the oxygen concentrations ranged from 0.01 - 0.22 pct. To prevent segregation and loss of oxygen

during sampling, either argon quenching or suction into a silica tube was used. Those were adopted after a comparative study of the sampling techniques in an effort to retain the equilibrium oxygen concentrations on rapid cooling. Sano and Sakao[15] from their data represented the solubility of oxygen in iron with this equation.

$$\log \left[\%\ \underline{O}\right]_{Al_2O_3} = \frac{-3,560}{T} + 1.19$$

which gives a value of 0.16% oxygen at 1530°C. The results of Sano and Sakao [15] are shown in Fig (2) along with the data of other investigators, as a plot of equilibrium constant vs oxygen content at 1550, 1600 and 1650°C. K_1' is shown as approximately a linear function of oxygen content. A study of all the available data on reaction (1) shows that the results of all the experimentors other than those of Fontana and Chipman[3], Samarin and Chipman[4] and Dastur and Chipman[5] indicate that K_1' decreased with increasing oxygen content, implying that iron-oxygen solutions do not conform exactly to Henry's Law. The relation between $\log f_o$ and temperature as given by Sano and Sakao[15] is:

$$\log f_o = \left(\frac{-1,750}{T} + 0.76 \right) \cdot \left[\%\ \underline{O}\right]$$

The data obtained by Sano and Sakao[15] are in good agreement with those of Gokcen[6] and of Averin, Polyakov and Samarin[14] in the low oxygen range and with the value of $\log f_o$

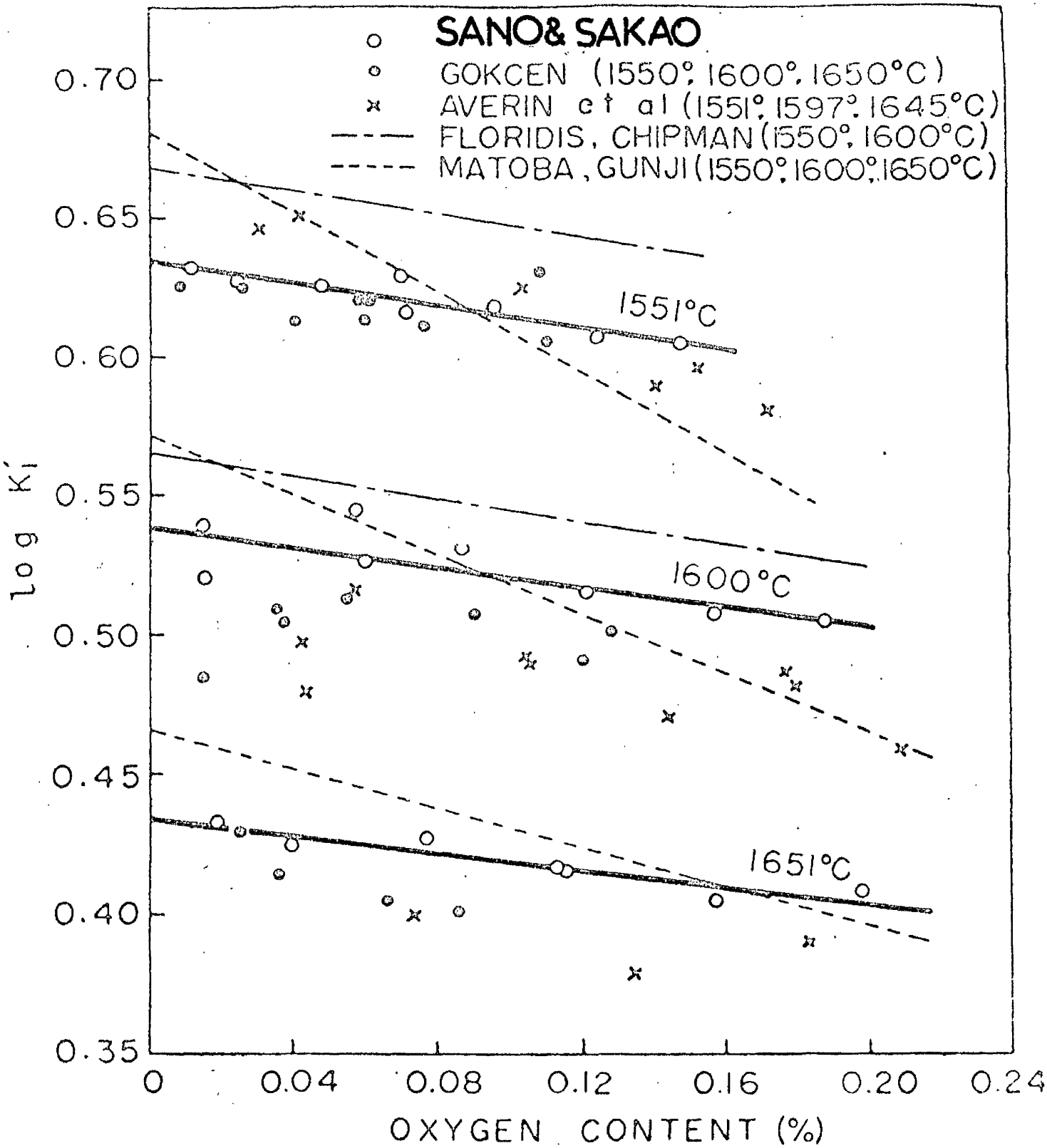


FIG 2 Effect of the oxygen content on the apparent equilibrium constant.

obtained by Floridis and Chipman[7] which is:

$$\log f_O = -0.20 \left[\% \underline{O}\right]$$

The effect of temperature on the equilibrium constant as given by the various workers is shown in Fig (3). The equilibrium constant $\log K_1$ can be determined by the extrapolation of $\log K_1'$ v $\% \underline{O}$ curve to zero per cent oxygen. The data obtained by Sano and Sakao[15] was represented by the equations:

$$K_1 = \frac{pH_2O}{pH_2 * \underline{O}}$$

$$\log K_1 = \frac{7,040}{T} - 3.224 \quad \ldots\ldots\ldots\ldots (6)$$

$$\Delta G^O = -32,210 + 14.75\ T$$

The data obtained by Sano and Sakao[15] are in good agreement with the data of Floridis and Chipman[7] Matoba[13] and Gokcen[6] at all oxygen concentrations, and with Averin, Polyakov and Samarin[14] in lower oxygen concentrations.

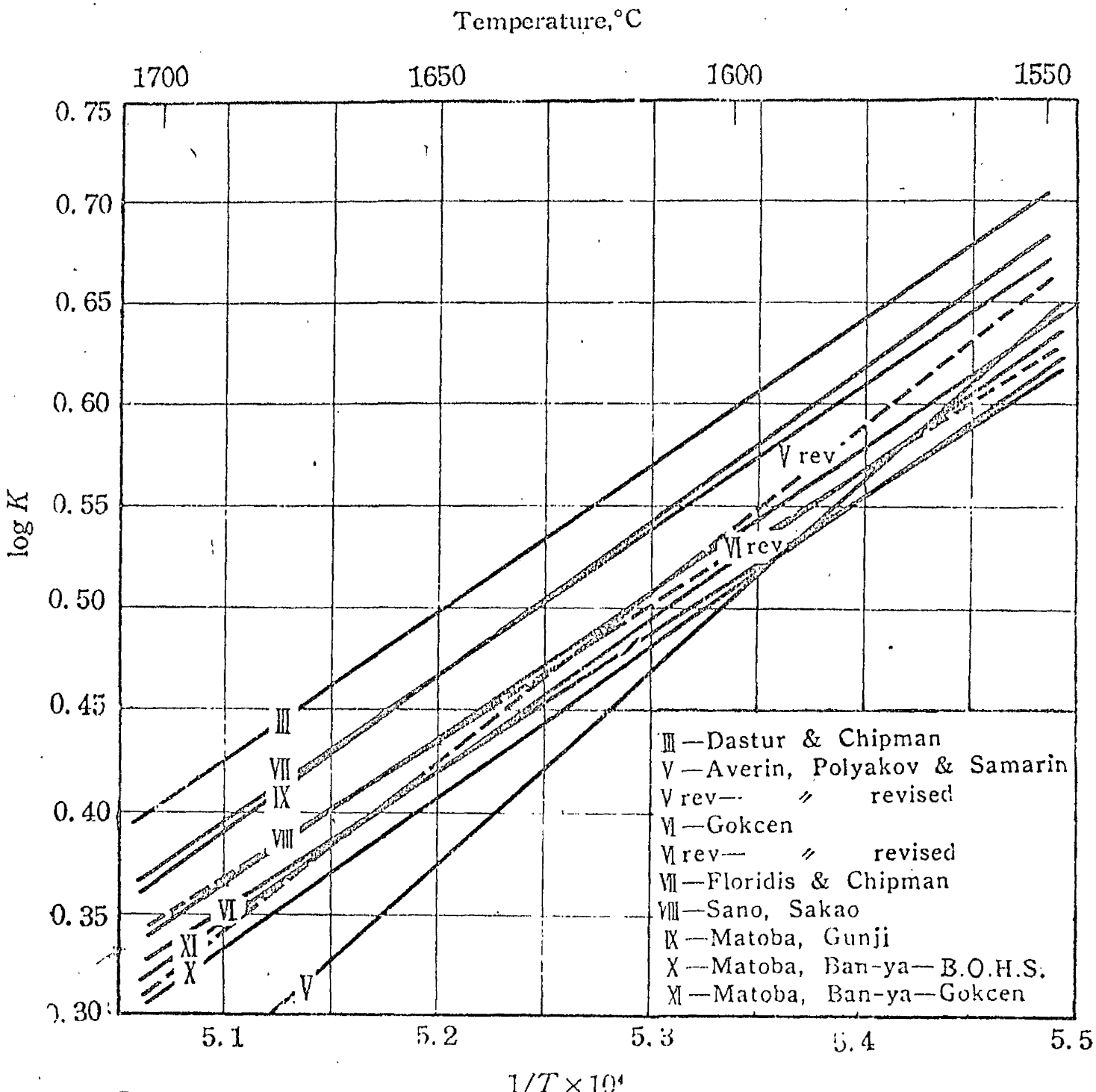


FIG 3 EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT FOR THE REACTION

$H_2 + O = H_2O$

(2) IRON-CHROMIUM SYSTEM

A number of investigations have been carried out to determine the thermodynamic properties of the Fe-Cr system. There is considerable disagreement among the existing data on this system, both in the liquid and solid states. The iron-chromium phase diagram first investigated experimentally by Adcock[16] and later reviewed by Hallawell[17] is shown in Fig. (4).

Due to the similarities in the atomic size and other properties between chromium and iron, it has been suggested[18, 19] that they form ideal solutions both in liquid and solid states. This assumption was also based on the absence of intermetallic compounds and the wide range of solid solubility of chromium in α-Fe.

Chen and Chipman[20] assumed in their experimental investigation, that liquid iron-chromium alloys behave ideally. They[20] had studied the equilibrium between chromium and oxygen in liquid iron at 1600°C, using a controlled mixture of water vapour and hydrogen.

Later Lyubimov and Gronovskaya[21] employed a method using radioactive chromium for the determination of vapour pressure of chromium in liquid iron-chromium alloys. From the vapour pressure obtained, the activities, the activity coefficients and other thermodynamic properties were calculated in the ranges of

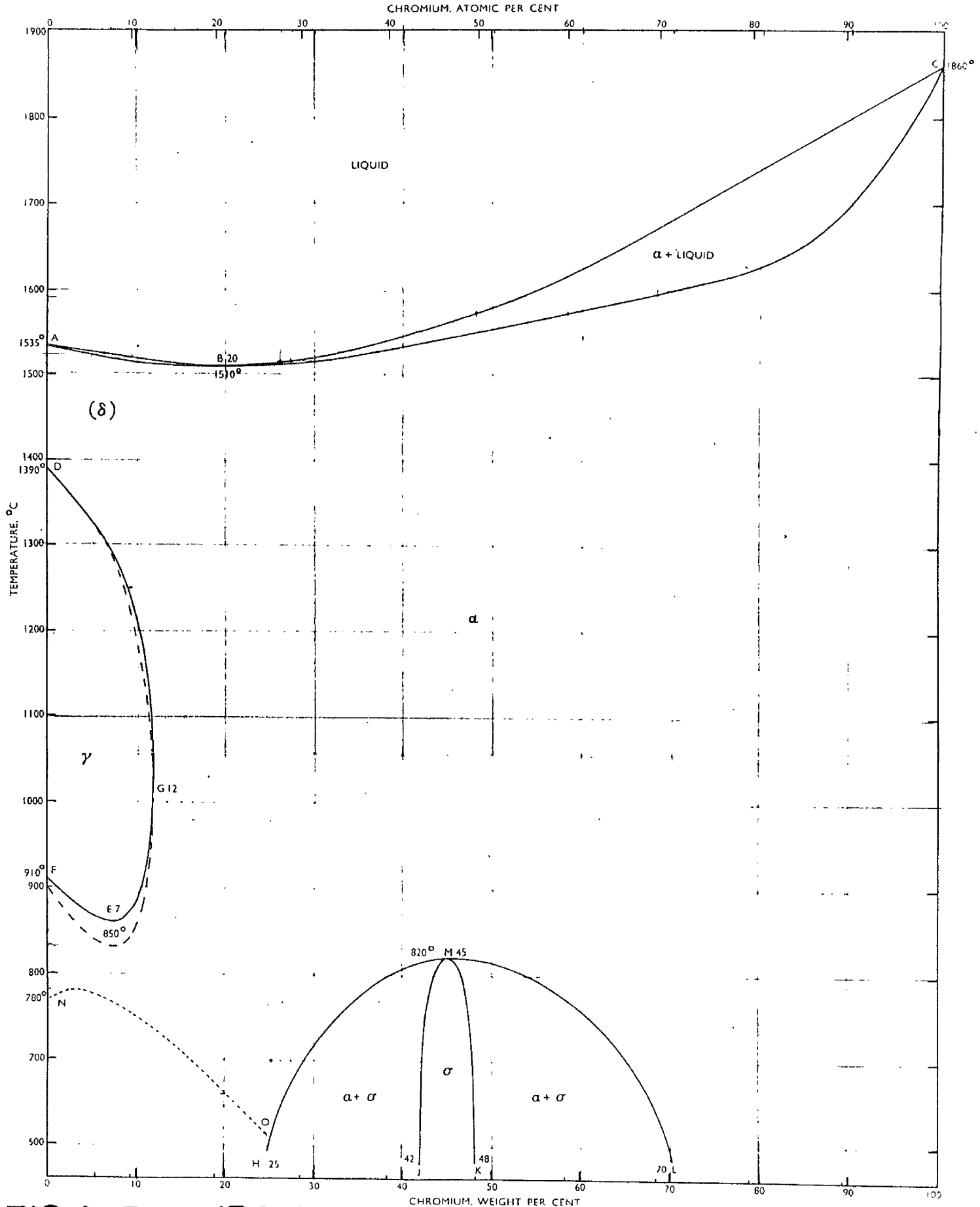


FIG 4 THE IRON-CHROMIUM PHASE DIAGRAM

temperature (1670 - 1824°C) and concentrations (1.89 -63.19 atomic per cent chromium) studied. They[21] found a slight positive deviation from the Raoult's Law in the liquid iron-chromium system.

Wada, Kawai and Saito[22] have measured the activities of chromium in the liquid iron-chromium system at 1630°C upto about 40 atomic per cent chromium by a vaporisation method using radioactive chromium. In their[22] method high purity iron-chromium alloys containing radioactive chromium were degassed and heated to 1630°C in alumina crucible. The vapours were condensed on a target for 16 minutes. The duration of condensation was fixed throughout the experiments. The ratio of the amount of metal condensed to the total amount of metal evaporated was regarded constant, because the conditions were kept the same in all the experiments. The radioactivity of the chromium in the condensate was measured by a scintillation counter. From the above measurements, the relative amount of chromium evaporated from the unit area of the surface of the sample was calculated. This was proportional to the vapour pressure of chromium, viz., to the activity of chromium in the molten alloy. They[22] found from their results that iron-chromium system could be regarded as a regular solution, showing a negative deviation from the Raoult's Law.

Recently, Cheriton[23] has studied the equilibrium between chromium and oxygen in liquid iron at 1600°C using a hydrogen/water vapour mixture to control the oxygen potential of the gas phase.

From his[23] results he calculated the chromium activities on the basis of chromic oxide as the oxide phase in equilibrium with iron-chromium alloys and hydrogen/water vapour mixture. His[23] results showed a small negative deviation from ideality upto 14% Cr and above this chromium concentration a large positive deviation from ideal behaviour was observed. His[23] experimental results could also be explained on the basis that the oxide phase in equilibrium with Fe-Cr alloys and hydrogen/water vapour mixture has a variable composition, which means that the activities cannot be calculated, because the free energy of formation of the chromous oxide is not available from the thermal data. Similarly from the present work the activities could not be calculated. This will be discussed later.

Various workers have different views on the thermodynamics of solid Fe-Cr alloys. Matveyeva and Ivanov[24] from their data in the temperature range of 1100 - 1250°C have shown a negative deviation from the ideality.

McCabe and co-workers[25] have measured the activities of iron and chromium using a Knudsen Cell. From the weight losses, the vapour pressure of chromium were calculated. It was observed from their results at 1200 - 1250°C that the system shows a maximum positive deviation from the Raoult's Law of 19 pct. At the minimum in the phase diagram of the Fe-Cr system the composition of the liquid and solid are the same, thus the presence of Cr in

equilibrium with the liquid and solid will be the same at this composition and from knowledge of the a_{Cr} in the solid solution the a_{Cr} in the liquid phase may be deduced. The data of McCabe[25] shows a maximum deviation of 19% from ideality in the solid alloys at 1207°C and if this deviation is present at the minimum (1510°C) then the liquid solution would be ideal at this composition. If, as is more likely, the deviation in the solid solution decreases with temperature then there will be a negative deviation from ideality in the liquid solution, in the extreme, assuming the solid solution to be ideal, the liquid solution would exhibit a 19% negative deviation.

Kubaschewski and Heymer[26] measured the vapour pressure of chromium by coupling the Knudsen effusion method with Tracer analysis in order to increase the sensitivity of measurement in iron-chromium alloys. The chromium pressures in the Fe-Cr system have been measured at 1340 - 1370°C for various composition. From vapour pressure measurements the activities of chromium were calculated. This data on the activities show a small positive deviation from the Raoult's Law and is in good agreement with the previous work of McCabe et al.

Vintaikin[27] has also measured the activity of chromium in iron in the solid state and large positive deviations from ideality are reported.

In a more recent investigation by Jeannin, Mannerskantz and Richardson[28] measurements have been made in the temperature range of 1040 - 1300°C of the equilibrium between

$$Cr_2O_3 + 3H_2 \rightleftharpoons 3H_2O + 2\,Cr$$

with pure chromium metal and with chromium alloyed with iron. From the work with Fe-Cr alloys, the chromium activities were derived using the relationship:

$$a_{Cr} = \left[\left(\frac{pH_2}{pH_2O} \right)_{alloy} \Big/ \left(\frac{pH_2}{pH_2O} \right)_{chromium} \right]^{\frac{3}{2}}$$

The compositions of the alloys studied ranged from 2 wt. percent to 30 wt. percent. The technique employed was to circulate hydrogen in a closed system over a mixture of oxide and alloy or oxide and metal and to measure the partial pressure of water vapour developed in the gas when the system had come to equilibrium. The results[26] show substantial positive deviations from ideality and also confirm the results obtained by Kubaschewski and Haymor[26] and McCabe[25] rather than those of Vintaikin.[27]

(3) IRON-CHROMIUM-OXYGEN SYSTEM

The alloying element chromium has weak deoxidising properties and its reactions with oxygen in liquid iron-chromium alloys are of interest. It is known of course, that chromic oxide is moderately stable at steel making temperatures. It is not stable enough to make the element a good deoxidiser, but is sufficiently stable to lead to the formation of chromic oxide and chromite inclusions in most steels, which contain significant amounts of the alloys.

Studies of the non metallic inclusions have indicated that there are at least two products of reaction of chromium with dissolved oxygen.

(1) Chromic oxide, Cr_2O_3

and

(11) Chromite, $FeO.Cr_2O_3$

The conditions which lead to the formation of the one or the other product are not clearly defined.

Chen and Chipman[20] experimentally observed the conditions of equilibrium in the two reactions:

$$2\,\underline{Cr} + 3\,\underline{O} \rightleftharpoons Cr_2O_3$$

$$Fe + 2\,\underline{Cr} + 4\,\underline{O} \rightleftharpoons FeO\,Cr_2O_3$$

The essentials of their experimental technique were to melt iron-chromium alloys in chromite or chromic oxide crucibles and to bring the melt into equilibrium with a controlled atmosphere of hydrogen and water vapour, thus controlling the oxygen potential in the melt. It was expected that the chromium content of the bath would adjust itself to the equilibrium concentration by reacting with oxygen if it was in excess or by the solution of part of crucible, if the bath was deficient in chromium. The experiments were carried out in an induction furnace. In order to cut down thermal diffusion due to temperature gradient, the gas mixture was preheated to 1100°C. Temperature measurements were made with an optical pyrometer and it was stated by the workers[20] that an error could be introduced due to the higher emissivity of higher chromium alloys. For the high chromium heats it was found necessary to melt under hydrogen, since water vapour tended to form a solid film around the chromium metal, thus prolonging the time needed for melting. Low chromium heats were melted under the desired gas mixture since chromic oxide dissolved readily under hydrogen atmosphere. It was also thought that the equilibrium should be approached from both the high chromium and low chromium sides, but practically no reliable data could be obtained from the high chromium side due to the formation of the solid film over the surface of the melt. It was observed that a melt with a 4% chromium could

be obtained from a pure iron charge by keeping it for only 1 hour at 1595°C. From this it was concluded

1) That the solution of chromic oxide was not a slow process and that the equilibrium could be reached within a reasonable length of time, if amount of chromium charged was not too low, and

11) That although all the results were obtained from the lower chromium side, they could be counted on to represent the equilibrium conditions.

Microscopic examination and X-ray diffraction analysis of the solid inclusions showed the presence of chromite and chromic oxide only. It was also stated that slight amount/s of other substance/s might occur in the solid phase as solid solutions, but if the assumption that the solubility was limited was true, the activity of the solid phase could be considered as constant and equal to that of the solid chromite or chromic oxide.

The product of deoxidation at 1595°C was identified as chromite ($FeO.Cr_2O_3$) in low chromium range (5.% max) and as chromic oxide (Cr_2O_3) in high chromium steels. This statement is supposed to be true only when the oxygen in the metal is exactly in equilibrium with the stable non metallic phase. If oxygen is in much excess, the precipitation of both chromite and chromic oxide could be possible. When chromite was the stable solid phase, the reaction involved in the system was

$$FeO.Cr_2O_3\ (s) + H_2\ (g) \rightleftharpoons H_2O(g) + Fe(l) + 2Cr \qquad \ldots\ldots\ldots\ldots(a)$$

(where "s" denotes solid state, "g" gas state and "l" liquid state)

It was assumed that $FeO.Cr_2O_3$ was a pure solid phase, that the activity of iron was constant, and that the activity of chromium was proportional to its weight percent. The equilibrium constant for the above reaction was then:

$$K = \left\{ \frac{pH_2O}{pH_2} \right\}^4 . \left[\%Cr \right]^2$$

Similary, when chromic oxide was the solid phase, the reaction and equilibrium constant was:

$$Cr_2O_3 (s) + 3H_2 (g) \quad 3H_2O (g) + 2\underline{Cr} \quad \ldots\ldots\ldots (6)$$

$$K = \left\{ \frac{pH_2O}{pH_2} \right\}^3 . \left[\%Cr \right]^2$$

The equations for the equilibrium constant for reaction (a) and (b) when written in logarithmic forms are:

$$\log \left\{ \frac{pH_2O}{pH_2} \right\} = \frac{1}{4} \log K - \frac{1}{2} \log \left[\% Cr \right]$$

and

$$\log \left\{ \frac{pH_2O}{pH_2} \right\} = \frac{1}{3} \log K - \frac{2}{3} \log \left[\% Cr \right]$$

From their experimental results Chen and Chipman[20] showed that in the range 0-5.5% Cr, Chromite was the equilibrium phase and the slope of the logarithmic curve was $-\frac{1}{2}$ while in the range 5.5 - 22% Cr chromic oxide was the equilibrium phase and the slope of the logarithmic curve was $-\frac{2}{3}$. Later when Chipman[29]

reviewed this work in the light of investigations[30] on the oxide phases in the Fe-Cr alloys it was considered that in the range 10-22% Cr, the slope of the curve was steeper and it corresponded to a solid phase of composition Cr_3O_4. It was further suggested that in the Cr_3O_4 range the data would be better served by a line of steeper slope c.f. one corresponding to CrO.

Similar studies on the Fe-Cr-O equilibria were later carried out by Lincsinskii and Samarin[31], Turnbogen[32] and Charlton[23].

Lincsinskii and Samarin[31] in their study of the system equilibrated iron-chromium alloys with water vapour and hydrogen mixture. Alumina crucibles were used and thus the equilibrium was approached by oxidising chromium out of the melt. The equilibrium was considered to have been attained as soon as an oxide phase appeared on the melt surface. This is not quite true as it might have been necessary to oxidise considerable amounts of chromium from the melt for a particular gas composition before a true equilibrium was attained. From this point of view it may be considered that if their results are subject to error it will be due to high chromium contents. As no other experimental details were given, it is not known if adequate precautions against thermal diffusion were taken. The equilibrium equation was expressed in a general form and an attempt made to evaluate "x" experimentally.

$$Cr\ O_x + H_2 \rightleftharpoons x\ H_2O + \underline{Cr}$$

$$K = \left\{ \frac{pH_2O}{pH_2} \right\}^x \cdot [\% Cr]$$

$$\log K = x \log \frac{pH_2O}{pH_2} + \log \% Cr$$

Turkdogan[32] has studied the reaction:

$$Cr_2O_3\ (s) + 3H_2\ (g) \rightleftharpoons 3H_2O\ (g) + 2\ \underline{Cr}$$

$$K = \left\{ \frac{pH_2O}{pH_2} \right\}^3 \cdot \frac{[\% Cr]}{aCr_2O_3}$$

In his[32] experimental technique, iron-chromium melts were held in recrystallised alumina crucibles and equilibrated with hydrogen/water vapour mixture. The gas mixture was diluted with argon in the argon/hydrogen ratio of 4 : 1 and preheated to 1600°C to avoid thermal diffusion. The composition range studied was 3 - 12 pct. of chromium. In all the experiments the equilibrium was approached from the high chromium side, i.e. by oxidising some chromium out of the melt. To ensure that the molten metal was exposed to the gas phase for rapid establishment of equilibrium gas and initial chromium contents were adjusted so that only a small amount of chromic oxide was formed and thus floated freely on the top. Each experiment was continued for 2 hrs. after the appearance of slag on the melt. At the end of the experiment, the reaction tube

was flushed with argon and a sample taken using a silica tube Taylor Sampler and quenched in water. The oxygen determination were made by the vacuum fusion method. Turkdogan's[32] results give lower values for equilibrium chromium concentrations as compared with the data of Chen & Chipman.[20]

In the investigations (20, 31, 32) discussed previously the behaviour of chromium in iron was assumed ideal and any changes in thegradient in the log $\frac{pH_2O}{pH_2}$ v log Cr plot were supposed to be due to changes in oxide phase. Ignoring that part of Linoznakii and Semerin's[31] work (above 16% Cr) which have been found to be theoretically unsound, all the three investigations have concluded that equilibrium with chromite and then chromic oxide is involved.

Charlton[23] in a more recent study of chromium-oxygen equilibria in liquid iron at 1600°C has suggested that iron-chromium solutions cannot be regarded as ideal solutions. Upto 14 pct. chromium a negative deviation from Raoult's Law was reported. A wide range of chromium concentrations were investigated. In his[23] experimental technique iron-chromium alloys were equilibrated with hydrogen/water vapour mixtures in either chromite or chromic oxide crucibles. The experiments were carried out at 1600°C in a molybdenum wound resistance furnace. The temperature measurements were made

using a 5% Rh Pt/20% Rh Pt thermocouple. The gas mixture was bubbled through the melt to hasten the approach to equilibrium and also to eliminate the possibility of thermal diffusion. Experiments were continued for about 4 hrs. and sometimes even longer periods when the chromium content was high or oxygen potential low. Equilibrium was approached both from the low chromium and high chromium sides. Several experiments were made to find each equilibrium point. At the end of an experiment a sample was taken using a silica tube Taylor Sampler, after flushing the reaction tube with argon. The samples were quenched in water. The oxygen estimations were made by the vacuum fusion method.

Charlton's[23] results show equilibrium with chromite in the range 0 - 3% chromium. From 3 - 10% chromium his results show a continuous change in the gradient of the curve, indicating replacement of iron by chromium. From 10 - 24% chromium he has shown a slope of minus one from his results, but in fact his results in this range (10 - 24% Cr) suggest a slope of - 1.5.

A brief comparison of the various data is shown in Table (1), where the free energy of formation of different oxides of chromium as found in the various works is given. The values are all given at 1600°C, the pure substance being taken as the standard state.

TABLE (1)

NAME	REFERENCE	$-\Delta G_{1600°C}$ Cals
$FeO.Cr_2O_3$	Chun & Chipman[20]	196,000
	Charlton[23]	194,500
	Kubaschewski[32]	200,700
	Lukashenko & Semarin[31]	188,400
	Dworkin & Bonnickson[33]	199,080
Cr_2O_3	Chun & Chipman[20]	152,250
	Charlton[23]	-
	Kubaschewski[32]	158,500
	Lukashenko & Semarin[31]	146,250
	Thermal data[34]	155,700
Cr_3O_4	Kelley et al[20]	-
CrO	Chipman[29]	51,500
CrO	Charlton[23]	52,400

A review of the previous investigations on the Fe-Cr-O system however indicates that some of the workers have considered the assumption of $FeO.Cr_2O_3$ and Cr_2O_3 inclusions only, as inadequate to explain their results. It is therefore, strongly suspected that some other oxides of chromium may be involved. Since $FeO.Cr_2O_3$ and Cr_2O_3 are the most stable oxides of iron and Chromium at low temperatures, direct observation of other possible phases has been difficult and their existence and specific identities have been largely a matter of speculation or inference.

Hilty[35] in rationalising his observations of the relation between carbon and chromium in molten iron under oxidising conditions suggested "CrO" as the oxide phase involved on the basis that the equation

$$CrO + C \rightleftharpoons Cr + CO$$

fits the observations quite well without complications.

Dennis and Richardson[36] disagreed and presented calculations purporting to show that Hilty's[35] results could be predicted from the activities of chromium and carbon and the assumption of Cr_2O_3 as the stable phase.

Chipman[29] in revising the previous work of Chen & Chipman[20] summarised his observations with the statement that at 1595°C, chromite was the stable phase in equilibrium with melts containing less than 3% Cr and that there was a continous change in the gradient of the curve in the range 3 - 10% Cr and at higher Cr concentrations in

the metal Cr_3O_4 became the stable phase.

Sims, Beller and Boulger [37] reviewed Chen and Chipman's[20] observations, and attempted to explain their oxygen solubility results by assuming a homogeneous metal phase containing "CrO". They suggested that chromite and Cr_2O_3 inclusions observed to contain islands of metal, could form by the precipitation and disproportionation of dissolved CrO. Zapffe[30] also discussed the possible formation of Cr_2O_3 by disproportionation of CrO. Linevinskii and Samarin[31] recognised only chromite and chromic oxide as the solid phases in equilibrium with the metal, but postulated that at chromium concentrations above 16 pct. in the metal, CrO is formed as an entity dissolved in the metal, though not existing as a separate phase, a hypothesis which is very doubtful.

Hilty, Forgeng and Folkman[30] made a detailed study of the composition structure and properties of the oxide inclusions. It was considered that with sufficiently rapid cooling, the primary inclusions are representative of the oxide phases in equilibrium with the metal at the time of solidification. A comparison of the structure of the inclusions in rapidly cooled heats with those in heats cooled at a slower rate was also made to determine how the primary inclusions may be modified by subsequent reaction or transformation. The characteristics of the inclusions were studied at various chromium contents by microscopic examination and X-ray diffraction investigation of the inclusions isolated from the metallic matrix

by electrolysis of the samples. Polarized light was used to determine the true transmission colour as well as the presence of inclusions.

The categories of alloys were arbitrarily placed as follows:

1)	Low chromium	0 - 3 pct. Cr
2)	Medium chromium	3 - 9 pct. Cr
3)	High chromium	9 - 25 pct. Cr
4)	Very high chromium	over 25 pct. Cr.

In the low chromium alloys, the inclusions were of the chromite type. X-ray diffraction analysis showed a simple cubic structure of the spinel type i.e. $FeO.Cr_2O_3$. The inclusions in the medium range were similar to those in the low chromium heats, except that they had a variable axial ratio which appears to have resulted from a distortion of cubic spinel structure. The inclusion in the high chromium level had a structure with an almost constant axial ratio. The chemical analysis of this phase approximates that of the compound Cr_3O_4 with a small amount of iron substituting for chromium. At very high chromium contents, the Cr_3O_4 phase appeared to be the only primary inclusion. This phase has the tendency to disproportionate at lower temperatures as:

$$3\ Cr_3O_4 \longrightarrow Cr + 4\ Cr_2O_3$$

for both the Fe-Cr-O alloys and in oxygen saturated pure chromium.

Further it was proposed that Cr_3O_4 form by a peritectic reaction between Cr_2O_3 and the liquid.

On the other hand, Hook, Garret and Adair[39] found in their investigations of impurity phases formed in pure chromium that Cr_3O_4 formed intergranularly and was stable as low as 1500°C which is well below the melting point of chromium. A further investigation by Hook and Adair[40] indicated that Cr_3O_4 undoubtedly occurred in pure chromium as low as 1300°C. It was emphasized that the system they examined (a relatively pure chromium metal containing as major impurities)

Fe	=	135 p.p.m.
Si	=	20 - 100 p.p.m.
O	=	35 - 137 p.p.m.

does not appear to be a simple binary with respect to chromium and oxygen. Rather the observed co-existence of the two oxides of chromium under the experimental conditions employed was said to indicate that the system was at least ternary. It was stated that in order to have observed the three phase equilibria, at least one of the oxides, Cr_2O_3 or Cr_3O_4 must not be a pure binary oxide. A residue found by X-ray diffraction to be entirely Cr_3O_4, was analysed by emission spectroscopy and was found to contain about 10 wt. pct. Fe.

It was been suggested by Hook et al[40] from the work of Hilty et al[30] and the presence of iron as a major impurity in chromium in their work[40] and also in nearly all "pure" chromium,

that iron is responsible for the observed ternary equilibrium among the oxides.

Kramers and Smith[41] in their study of the properties of non-stoichiometric oxides, have not found any evidence for the "CrO" in the pure two component systems. It was however, noticed that in all the chromium preparations, some volatilisation occurred but it was difficult to confirm the chemical composition by subsequent chemical analysis.

Tasche[42] has studied the chromium distribution between metal and slag at different oxidation levels and the following reaction was considered relevant.

$$[Cr] + (FeO) \rightleftharpoons (CrO) + [Fe]$$

Some recent investigations have been carried out to find the composition of the non-metallic phases in equilibrium with Fe-Cr alloys, the nature of chromium distribution in the slags and the reduction path of Cr_2O_3 to Cr, in an effort to know more precisely the true deoxidation product in the Fe-Cr-O system.

Strator and Mantell[43] have studied the kinetics of hydrogen reduction of chromic oxide and found that Cr_2O_3 was reduced directly to chromium without forming the intermediate oxide, CrO, which was not a stable phase in the reduction of Cr_2O_3 to chromium over the temperature range 1130 - 1490°C. This

reduction path was confirmed by X-ray diffraction analysis. This is in agreement with the earlier work of Saeki[44] who reported that over a temperature range of 1000 - 2000°K Cr_2O_3 is more readily reducible to Cr than CrO.

Kojima and Sano[45] have studied the distribution of chromium between an acidic slag saturated with silica and a liquid Fe-Cr alloy. It was reported that when the chromium concentration was higher than 3 pct. that chromium in the acidic slag behaved like the chromous ion (Cr^{++}). In iron alloys of low chromium contents, it was found that when the chromium content was less than 3 pct, the oxidation - reduction reaction between chromium and iron in the two phases was represented by the following reaction:

$$4\,(FeO) + 3\,[Cr] \rightleftharpoons (Cr_3O_4) + 4\,[Fe]$$

Healy and Schottmiller[46] in their study of chromium oxide-silica slags at low oxygen pressure have reported that when an equimolar mixture of Cr_2O_3 and SiO_2 was treated with hydrogen in the temperature range of 1500 - 1600°C, copious amounts of steam were evolved, and a low melting liquid formed which could be quenched to a blue crystalline material having a distinctive X-ray diffraction pattern. It was also found that the identical material could be produced by heating intimately mixed finely divided Cr_2O_3, Cr and SiO_2 held in tungsten crucible under purified argon. This reaction

product is found to be chromous silicate (Cr_2SiO_4). It is unstable at room temperature since on slow cooling it disproportionates in whole or in part to Cr_2O_3, Cr and SiO_2. No evidence of the existence of CrO as pure substance was found in this investigation. The lower oxide appeared to occur only in combination with silica.

(4) ATOMIC INTERACTIONS IN MOLTEN STEEL.

Alloy steels are multicomponent systems, and it is to be expected that there would be interaction between the components. Probably the best basis for the organisation of experimental data is the interaction parameter concept devised by Wagner[47]. A simple mathematical treatment, which is correct for the infinitely dilute solution, forms a satisfactory basis for calculation concerning more highly alloyed steel.

Chipman[29] has shown that when a solvent metal 1, contains a number of solute metals, 2, 3, 4 etc, the activity coefficient of one of these, for example, f_2 may be expressed as a product of factors which represent the effect of each of the other components. Thus in a solution of mole fractions x_2, x_3, x_4 etc.

$$f_2 = f_2^1 \times f_2^3 \times f_2^4 \times \ldots\ldots\ldots \text{ etc.}$$

Here f_2^1 is the activity coefficient of 2 in the binary solution of mole fraction x_2. The following equivalent expression has been devised by Wagner[47].

$$\ln f_2\,(x_2, x_3, x_4, \ldots) = \ln f_2^0 + x_2 \frac{\partial \ln f_2}{\partial x_2} + x_3 \frac{\partial \ln f_2}{\partial x_3} + x_4 \frac{\partial \ln f_2}{\partial x_4} + \ldots$$

where the derivatives are to be taken for the limiting case of zero concentrations of all solutes, and higher order terms of a Taylor series are neglected.

The term $\ln f_2^o$ is made zero by taking the standard state at the infinitely dilute solution. The derivatives are represented by the symbols, , etc. defined as:

$$\varepsilon_2^{(2)} = \frac{\partial \ln f_2}{\partial x_2}$$

$$\varepsilon_2^{(3)} = \frac{\partial \ln f_2}{\partial x_3} \quad \text{etc.}$$

and the equation becomes:

$$\ln f_2 \,(\, x_2, x_3, x_4, \ldots) = x_2 \varepsilon_2^{(2)} + x_3 \varepsilon_2^{(3)} + x_4 \varepsilon_2^{(4)} + \ldots$$

For convenience a slight modification of this representation has been proposed by Chipman[29] so that concentrations may be expressed as weight per cent rather than the mole fractions.

$$\log f_2 \,(\, \%2, \%3, \%4, \ldots) = o_2^{(2)} \%2 + o_2^{(3)} \%3 + o_2^{(4)} \%4 + \ldots$$

$$= \log f_2^1 + \log f_2^{(3)} + \log f_2^{(4)}$$

$$o_2^{(3)} = \frac{\partial \log f_2}{\partial \%3} \quad \text{etc.}$$

Wagner[47] has also shown that a simple relation exists between the effect of component i on f_j and the effect of component j on f_i:

$$\varepsilon_i^{(j)} = \varepsilon_j^{(i)}$$

The relations between o and ε for two elements of atomic weights Mi and Mj in the solvent metal, iron are:

$$\rho_i^{(j)} = \frac{M_{solvent}}{(2.303)(100)M_j}\,\varepsilon_i^J = \frac{0.2425}{M_j}\,\varepsilon_i^J$$

(M = molecular weight)

The reciprocal relationship for this parameter

$$\rho_i^J = \frac{M_j}{M_j}\,\rho_j^{(1)}$$

An important but previously undiscussed aspect of the use of interaction coefficients is their variation with temperature. Daoly and Pholke[48] have shown from thermodynamic relationships that this variation is given by:

$$\frac{\partial \varepsilon_i^J}{\partial T} = \frac{-1}{RT^2}\left(\frac{\partial^2 H}{\partial x_i \cdot \partial x_j}\right)_{x_i = x_j = 0}$$

The derivative of the molar enthalpy is obtainable from heat of solution data. When the derivative of enthalpy with respect to mole fractions of the two dilute solutes is not a strong function of temperature, an extrapolation to temperatures other than those in the experimental range can be accomplished directly. If the above equation is written in the form:

$$\frac{\partial\, \varepsilon_i^J}{\partial\left(\frac{1}{T}\right)} = \frac{1}{R}\left(\frac{\partial^2 H}{\partial x_i \cdot \partial x_j}\right)_{x_i = x_j = 0}$$

then a linear variation with the reciprocal of the absolute temperature is indicated.

Although many solution models have been proposed, none of these has been found satisfactory for quantitative predictions of interaction parameters. To study the effect of added components on the partial molar free energy of others, only two theories have as yet been applied. One is the free electron theory and the other is based on a nearest neighbour lattice model.

Studies of gas solubilities in alloys led Wagner[47] to the formulation of a free electron theory. The basis of the theory is that when an added element dissolves as ions and electrons, if the ion-electron interactions are much stronger than the ion-ion interaction then the primary variable of importance is the free energy of electrons and the effect of added elements thereon. Based on this idea Wagner has derived a relationship between:

$$\varepsilon_i^J = \pm\sqrt{\varepsilon_i^i \cdot \varepsilon_i^J}$$

Both self interaction parameters must have the same sign if the result is to have any meaning. The sign of the result is determined from qualitative considerations of the relative effects of the additions on the electron/atom ratio. This means that for a given solvent, all the self interaction parameters should have the same sign. This has been found to be true only when the deviations from ideality are large.

Alcock and Richardson[49] however, have applied a similar model to the case of a ternary alloy in which one solute is somewhat more dilute than the other. They[49] have derived an equation

for the activity coefficient of a dilute solute, s, in an alloy of two metals X and Y. This equation

$$\ln \gamma_s (x + y) = N_x \ln \gamma_s (x) + N_y \gamma_s(y) - N_x \ln \gamma_x (x + y) - N_y \gamma_y (x + y) \quad (i)$$

was based on the assumption that the distribution of atoms in the solution is random, that the co-ordination number of all three types of atoms is equal and that the energy of interaction between atom pairs is independent of concentrations.

For the same model the following equation was also derived,

$$\left[\frac{\ln \gamma_s (x + y)}{N_y}\right]_{N_y \to 0} = \varepsilon = \ln \gamma_s(y) - \ln \gamma_s (x) - \ln \gamma_y (x) \quad (ii)$$

It was shown that with these equations, it was possible to predict with useful accuracy, the behaviour of dilute solutes in ternary solutions from data for the three binary systems concerned. The first equation was reasonably accurate in cases where the differences between $\ln \left[\gamma_s(x) / \gamma_x (x + y)\right]$ and $\ln \left[\gamma_s (y) / \gamma_y (x + y)\right]$ were less than unity. The second equation gave values of the interaction parameter , which were correct in sign but smaller than the measured values. It was suggested that these differences might be partly or entirely caused by clustering about the solute atoms, of that component of the alloy which interacted more

strongly with the solute. In an attempt to account for this behaviour, equations based on a quasi-chemical model have been derived by Alcock and Richardson[50] which are as below:

$$\left[\frac{\partial \ln \gamma_s (x+y)}{\partial N_y}\right]_{N_y \text{ or } N_x = 0} = \varepsilon = \frac{-z(k-1)}{N_x + kN_y} \qquad (iii)$$

and

$$N_x\left[\frac{\gamma_x (x+y)}{\gamma_s (x)}\right]^{\frac{1}{z}} + N_y\left[\frac{\gamma_y (x+y)}{\gamma_s (y)}\right]^{\frac{1}{z}} = \left[\frac{1}{\gamma_s(x+y)}\right]^{\frac{1}{z}} \qquad (iv)$$

where z = co-ordination number.

Orianí[51] has already indicated that the application of this model to binary metal mixtures is not very helpful, for it leads to free energies of mixing which are little different from those calculated with the regular solution model. The major source of error in the regular model is probably the assumption that the energies of interaction between atom pairs are independent of the composition of the solution. This error remains in the quasi-chemical model and in most cases is likely to be greater than any other error arising from the neglect of clustering. Nevertheless, in certain binary mixtures, particulary non metals in metals, the main error might conceivably arise from neglect of clustering, when there are great differences between the pair wise energies of interaction.

The values of $\mathcal{E}$ calculated from equation (ii) and (iii), for a case where the energies of interaction between the dilute solute and the two metals differ greately, can be compared.

From the data so far considered, the conclusion is that although the quasi-chemical equation (iv) appears to be a slight improvement on equation (i), it often falls short of accounting the measured values of $\mathcal{E}$. One or all the following would seem to be possible reasons for the discrepancies.

(a) The energies associated with the pairwise interactions between the atoms of the ternary may differ from those for the three seperate binaries.

(1) The solute solvent interactions may vary with the proportions of each solvent atom about the solute.

(2) The interactions between unlike neighbouring solvent atoms in the co-ordination shell around each solute atom may be different from those between unlike solvent atoms in the remainder of the solution. Experimentally (1) and (2) are not likely to be distinguishable.

(b) The co-ordination number for the solute Z_0 may be different from those for the other atoms of the solution.

(c) The number of strong pair wise interactions about any solute atom may be much less than the co-ordination number.

The most reasonable explanation seems to lie in (a(1)) and (a (2)).

Chipman and Gokcen[52] have shown that in the binary and ternary systems in which iron is the solvent, the interaction parameter vary in a periodically regular manner. Further, these parameters for the ternary systems decrease with increasing stability of compounds between the solute atoms. Thus e_O^M decrease with increasing tendencies of elements, M to form stable oxides. From investigation of the Fe-Cr-O system involving the use of H_2O/H_2 mixtures, the interaction coefficient, ϵ_O^{Cr} can be calculated directly from the observed oxygen concentration.

The chromium-oxygen parameters at 1600°C as calculated by different workers using the above technique are given in Table (8).

TABLE 2.

Chromium Oxygen Parameters at 1600°C

Author	Parameter $e_O^{Cr} = \partial \log f_O^{Cr} / \partial [\%Cr]$	$\varepsilon_O^{Cr} = \partial \ln f_O^{Cr} / \partial N_{Cr}$
Chon & Chipman[20]	-0.041	-8.8
Turkdogan[32]	-0.064	-13.7
Cheriton[23]	-0.058	-12.4

EXPERIMENTAL PROCEDURE

EXPERIMENTAL PROCEDURE

(1) THERMAL DIFFUSION

Experimental studies of the composition of gaseous mixtures in equilibrium with a metal and its oxide at high temperatures have been extensively used in determining the free energy of oxides. In most of these investigations the results have been subject to errors or uncertainty on account of partial separation of the gases in a temperature gradient. A uniform mixture of gases of unlike molecular weight, flowing through any apparatus which is not at the same temperature throughout, tend to become non-uniform in composition in each temperature gradient. In general, the heavier gas tends to move toward the cooler and the light towards the hotter zones. This phenomenon of thermal diffusion was first predicted by Enskog[53] in 1911, and independently by Chapman[54] in 1916. It was observed for the first time by Chapman and Dootson[55] in 1917. In his work on the kinetic theory of gases, Chapman has shown mathematically that a temperature gradient in a mixture of two gases is in general sufficient to produce a partial separation. Later Gillespie[56] developed a simple theory of thermal diffusion based on elementary kinetic considerations in which

it was shown that the relative separation of two gases by thermal diffusion was inversely proportional to the square root of the mean molecular wt. of the mixture and could therefore be decreased by the addition of a third gas of high molecular weight.

Emmet and Shultz[57] discussed in detail the effect of thermal diffusion on the results of measurements by the static method, of the equilibrium $H_2O = H_2 + Fe = FeO$ in which case the error introduced in some reported H_2O/H_2 ratios was as great as 40%. Darken and Curry[58] measured the amount of thermal separation in gaseous mixtures flowing into or out of a vertical tube furnace and described conditions for avoiding error in this kind of system. It was stated that upward flow of the gas mixture in such a work was decidedly preferable to downward flow when it was desirable to minimise the composition inequality of the gas.

In earlier studies of equilibria involving oxygen in solution in a molten metal this source of error had been especially troublesome. The simplest method for stirring the melt and thus bringing it into equilibrium with the gas was to use high frequency induction heating. When a cold mixture of hydrogen and water vapour was blown over the surface of such a melt,

thermal diffusion opposed the approach of the heavier water molecule to the surface with the result that the surface layer of the gas was enriched in hydrogen and the molten metal contained oxygen below the concentration which would have been in equilibrium with gas of inlet composition. It was shown by Chipman and Fontana[3] that this phenomenon led to errors of about 20% in equilibrium constant at 1600°C, and that the errors could be at least partially eliminated by preheating the entering gases. Chen and Chipman[20] preheated the gaseous mixture to avoid thermal diffusion. Bastur and Chipman[5] concluded from their study that this error was eliminated by adequate preheating and the addition of argon in the approximate ratio of 4 : 1.

Floridis and Chipman also used the above treatment but increased the argon-hydrogen ratio to 6 : 1. McLean and Bell[59] in a study of the reaction

$$Al_2O_3 + 3H_2 \rightleftharpoons 3H_2O + 2\,Al$$

used preheat temperatures ranging from 1550 to 1650°C for experiments carried out at 1723°C and mixed the gas mixture with argon in the ratio of 1 : 6, to minimise the error arising from thermal diffusion. The results with and without preheat were compared and it was found that substantial errors were possible when the gas was not preheated.

One of the best methods to eliminate thermal diffusion although not very easy to perform, is to bubble the gas mixture into the melt. Gokcen[6] and later on Floridis and Chipman[7] used this technique to overcome thermal diffusion. Charlton[23] in a study of the Fe-Cr-O system had also used this technique quite successfully. He used a molybdenum wound resistance furnace, where the gases also got a considerable preheat.

In view of the previous investigations, it was considered safer to use the bubbling technique to avoid thermal diffusion, in the present work.

(ii) CRUCIBLES.

One of the basic requirements of high temperature research work is the choice and availability of a suitable container which can withstand the influence of the molten charge without having a contaminating effect on the equilibria being studied. Since in the study of Fe-Cr-O system, it was anticipated that either chromic oxide or iron chromite would be formed, it was desirable to use crucibles of these materials to avoid introduction of any foreign component. In the present work all the experiments were carried out in chromic oxide crucibles, which were made by a slip-casting technique.

The quality of plaster of Paris used for making the moulds was found to be very important for slip casting chromic oxide crucibles. It was found that the mould made from a coarser grade of plaster of Paris absorbed the water from the slip so rapidly that it resulted in the crucible cracking. Plaster of Paris of a finer grade suitable for making moulds was stirred into water in the approximate proportions of 4 parts by weight of Plaster to 3 parts of water. The thoroughly mixed mass was gently stirred to eliminate air bubbles and was then poured into a greased metal mould in which was suspended a greased brass former that was of the shape of the crucible. This brass former was slightly

tapered from top to bottom for easy removal of the slip cast crucible from the mould. The former and the metal mould were arranged to produce a plaster casting with uniform thickness. After the plaster of Paris had set, the former and the metal mould were taken off and the plaster mould was allowed to air dry for 2 - 3 days.

To make the crucibles, finely divided chromic oxide of a commercial grade used in paint and pigment industry was used. To impart necessary plasticity to the chromic oxide, it was mixed with 4% HCl solution and left for two days with occassional stirring to give the slip a proper consistency. To form a crucible, the slip was poured into the plaster mould without splashing or entrapping air. The plaster immediately began to absorb water from the slip, and a film of solidified material formed on the walls. The liquid level within the mould was maintained by addition of the slurry until the film of solidified material reached the desired thickness. The mould was then inverted and the residual liquid slip was poured out. The time required to form a crucible with a proper wall thickness varied with the consistency and acidity of the slip and with the condition of plaster mould. In the first 5 - 6 casts the time was not more than 10 - 15 minutes, but as the plaster got wetter, the crucible

formed slowly, hardened slowly and adhered to the mould because of slow absorption of the water and these crucibles were removed with difficulty from the moulds.

If the crucible formed properly, it remained in the mould when the excess of liquid slip was poured out, but it was too soft and plastic at this stage to support its own weight or to be removed from the mould. The crucible therefore was allowed to remain in the mould for further drying by absorption of water by the plaster and by evaporation from the inner surface of the casting. After about 1½ - 2 minutes the inner surface was dry enough to touch and the shrinkage cracks began to appear at the junction of the top of crucible and the wall of the mould. The casting then could be removed from the mould, particularly if the mould was gently tapped and rolled before it was inverted. The crucibles at this stage were somewhat plastic but were strong enough to be removed from the moulds without collapsing. After removing from the moulds, the crucibles were placed on a filter paper, where after ½ hr. air drying they were strong enough to be handled gently. They were air dried for overnight and then dried in an oven to about 150°C. Afterwards they were fired in a muffle furnace at 1000°C and finally at 1600°C in oxidising atmosphere, which made them quite strong and impervious to fluids.

(iii) MATERIALS

1. Chromium - Electrolytic lump chromium (Grade A) of the following analysis, as supplied by Union Carbide Company was used:

Cr	C	S	Si	Fe	O_2	H_2	N_2
99.9	.010	.006	.030	.020	.008	.0005	.016

2. Iron - The high purity electrolytic iron used had the following analysis.

Fe	C	S	Si
99.87	0.0101	.018	.003

3. Hydrogen and Argon used were of high purities.

(a) Hydrogen:

H_2 = 99.95%

O_2 = less than 10 v.p.m.

CO = about 10 v.p.m.

CO_2 = Nil.

other carbon compounds as CO_2 = about 20 v.p.m.

N_2 = 0.05%

(b) Argon:

Argon = not less than 99.99%

O_2 = 6 v.p.m.

N_2 = less than 30 v.p.m.

H_2 = less than 2 v.p.m.

carbon dioxide and carbonaceous compounds as CO_2 = less than 5 v.p.m.

(iv) APPARATUS.

The equilibrium apparatus used was similar to that described by Charlton[23] and consisted of two main parts.

1) Furnace

2) Gas train and the saturating unit.

FURNACE:

A molybdenum wound furnace as shown in Fig (5) was used to attain the desired temperature of 1700°C for this particular study. To hold the charge a reaction tube of recrystallised alumina having an internal diameter of 2" was used. This tube was impermeable to gases upto 1800°C. The reaction tube was surrounded and heated by an "Alper" alumina tube which was wound over a length of 16" with 18-gauge molybdenum wire and which in turn was surrounded by another commercial grade alumina tube. To avoid heat loss due to radiation, broken alumina chips were packed between the last two tubes. The whole assembly was held in a steel casing which was filled with high temperature insulating bricks. As molybdenum is very susceptible to oxidation, a molybdenum winding must always be heated in a neutral or reducing atmosphere. Every possible precaution was therefore observed to make all the joints completely gas tight. An asbestos gasket was put between the furnace lid and the main casing which were bolted together. This was further sealed from outside with a quick setting cement made from alundum and water glass. The

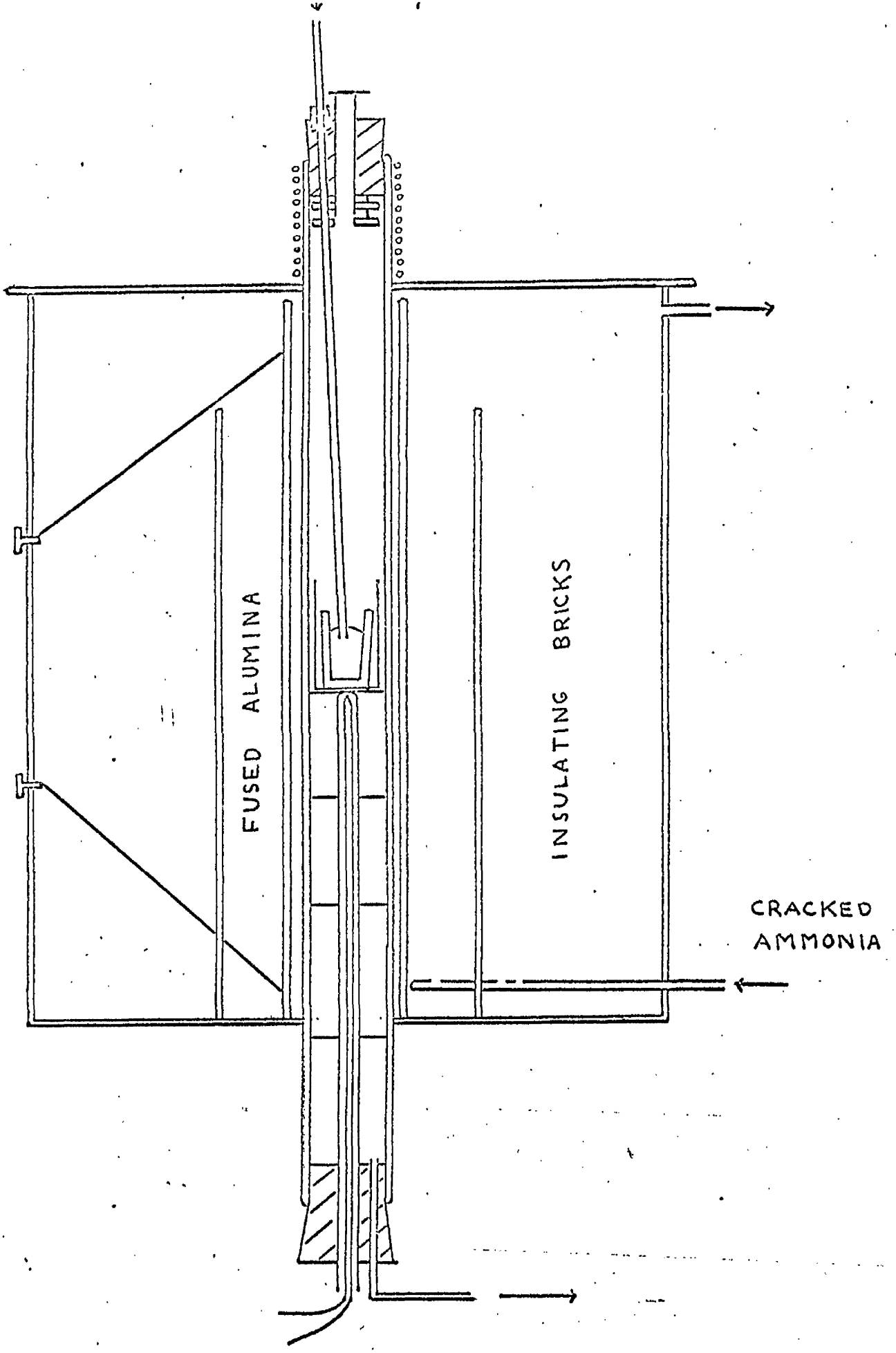


FIG 5 FURNACE

space between the reaction tube and the furnace casing at the top and bottom was made air tight by putting asbestos cords in between the two before bolting. Gas inlets and outlet provided at the bottom and top respectively were airtight. Dry cracked ammonia Fig (C) was passed into the furnace to give a slight pressure at the outlet end and ensured that cracked ammonia was passing out of the furnace rather than air leaking in.

The reaction tube was equipped with a rubber bung at either end. The upper bung contained a glass window and a brass gland through which passed an alumina tube. The gland was arranged to allow the tube to slide through it and still remain gas tight. To keep the top end of the reaction tube cold enough to hold the rubber bung, a 6" water cooled lead coil was fitted around the tube. The bung was further protected from the heat by fixing asbestos radiation shields underneath it. The lower bung, which held the alumina sheath for the thermocouple and supported alumina stools and the crucible, never got hot enough to need cooling.

<u>Temperature measurement.</u>

A 5% Rh Pt/20% Rh Pt thermocouple which was contained in an alumina sheath and rested directly beneath the charge was used for measuring the temperature. The E.M.F. developed was

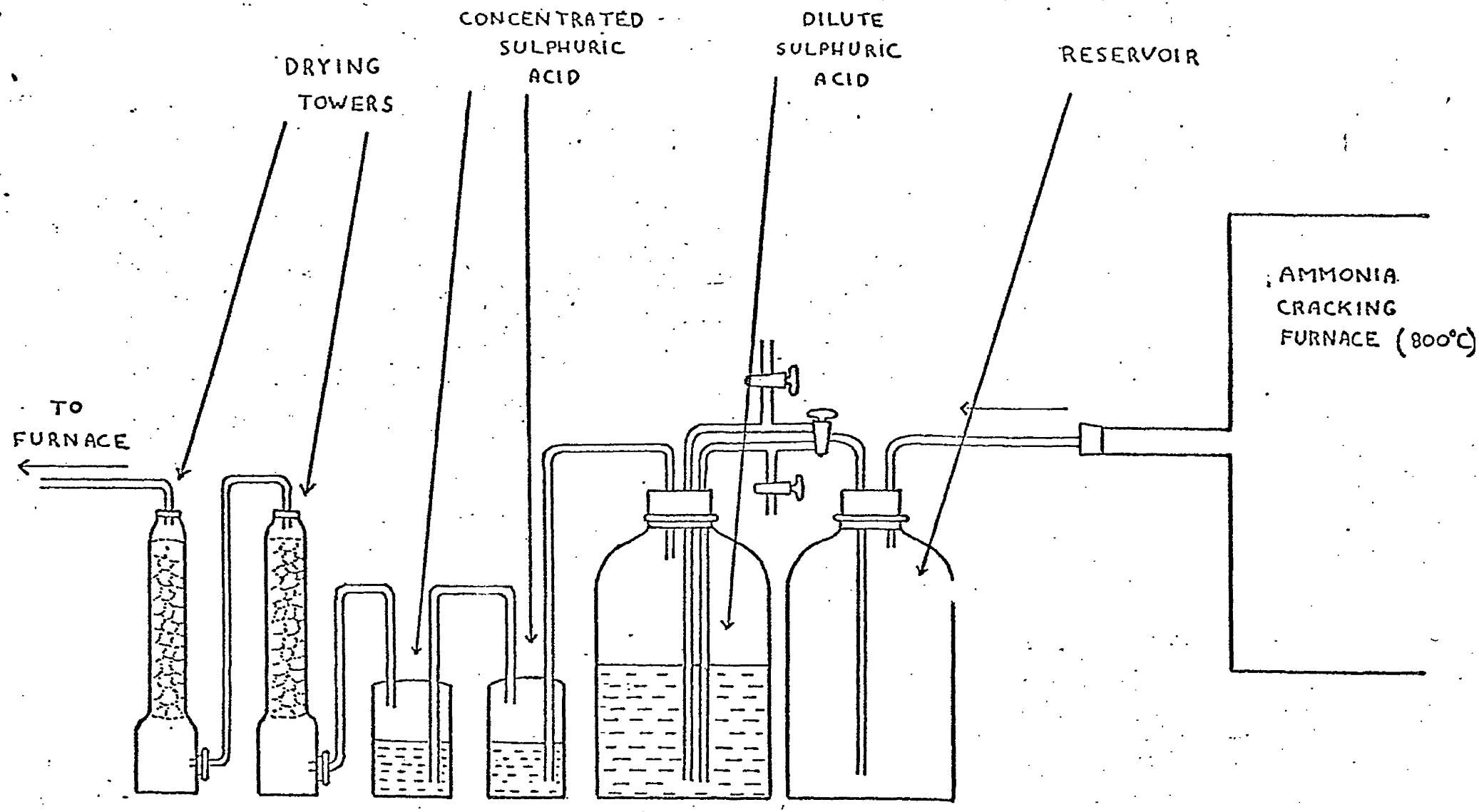


FIG 6 THE AMMONIA CRACKING TRAIN

measured by a Cambridge Workshop potentiometer. The alumina sheath had to be changed after every 4 - 5 experiments because it became porous and thermocouple deteriorated and broke under the reducing conditions encountered. The thermocouple was calibrated against the melting points of gold (1063°C) and palladium (1554°C). Under the experimental conditions used, automatic control of the temperature was not found successful. Therefore, the temperature was controlled manually by adjustments of the variac transformer. Once the steady conditions were attained, it was quite convenient to maintain the required temperature with only occasional slight adjustments of the variac. The hot zone of even temperature was about 2" long and extended the whole length of the molten charge. The temperature above the melt was also very high thus giving good preheating to the incoming gases.

Gas train and the saturating Unit.

Hydrogen and argon were supplied to the system through seperate calibrated flow meters. Before passing these gases to the furnace or to the saturator, they were dried by means of anhydrous magnesium perchlorate (anhydrone). A diagram of the gas supply train and the saturating unit is shown in Fig (7). The saturator unit consisted of three glass chambers (A) connected in series and all filled with distilled water. This unit was immersed in a water bath (B) which automatically controlled to the constant temperature (± 0.1°C) with a thermostat (C) having a

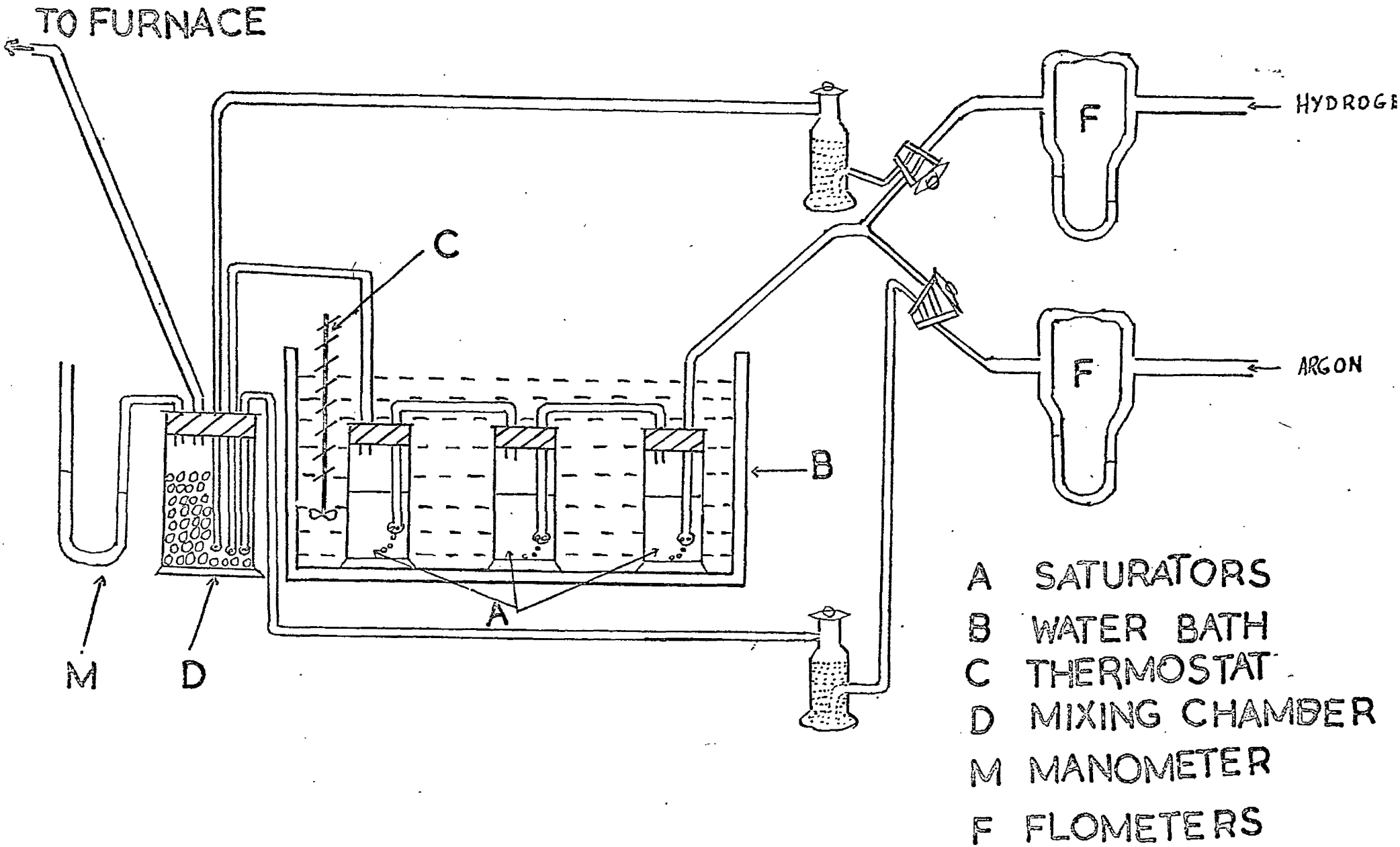


FIG 7 GAS SATURATING UNIT.

stirrer. The amount of water vapour picked up by the hydrogen depended upon the temperature of the bath. Outside this bath was another empty glass chamber (D) containing glass beads which helped to mix the gases. A glass mercury manometer (M) was also fitted to this chamber to see the pressure fluctuations when the gaseous mixture was being bubbled through the melt. From this chamber the gases were led to the furnace through a copper tube which was joined to the thin alumina tube through a piece of P.V.C. tubing, because rubber was slightly permeable to water vapours.

In the high chromium heats a mixture of oxalic acid dihydrate and anhydrous oxalic acid was used because of its low water vapour pressure, since its water vapour pressure ranges from about 1.5 m.m. at 18°C to 15 m.m. at 50°C. An ordinary water saturator required a thermostat bath operated below room temperature to yield water vapour pressure of less than 15 m.m. Hg. The saturator unit consisted of two tubes each 30 cm. long x 6 c.m. dia, containing anhydrone to dry the hydrogen, followed by a U-tube 75 cm x 1 cm. all filled with the mixture recommended by Baxter and Lansing[60] and Bookey and Tombs[61], viz 90% oxalic acid dihydrate and 10% of the anhydrous acid. There is very

good agreement among the vapour pressure - temperature data [60, 61] for COOH-COOH.$2H_2O$ mixtures and the data of Bookey and Tombs[61] was used in the present work. The data is given in Fig (6). Spot checks using a dew point meter confirmed the behaviour of the saturator.

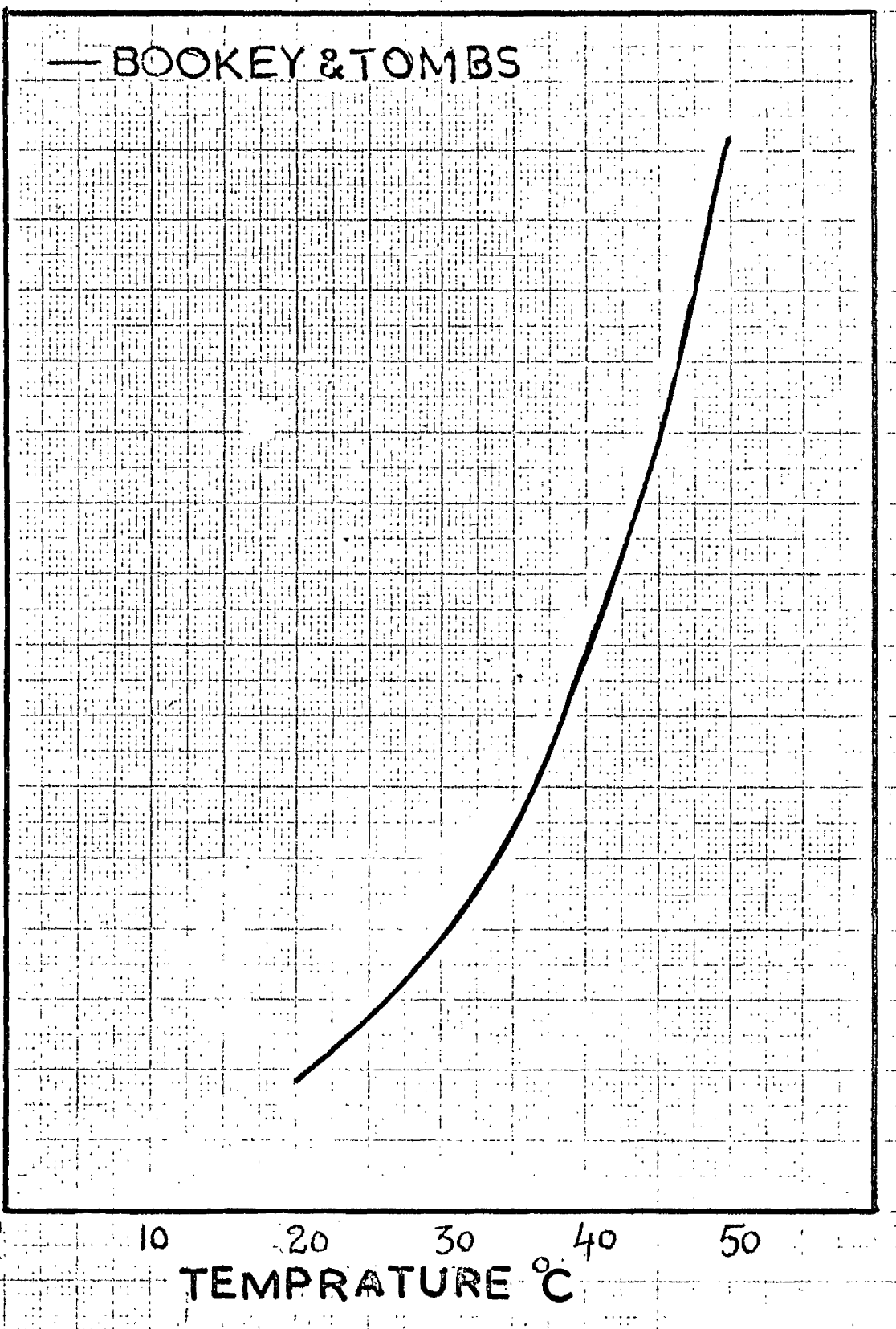


FIG 8 THE WATER-VAPOUR PRESSURE OF OXALIC-ACID-DIHYDRATE

(v) EXPERIMENTAL PROCEDURE.

To carry out an experiment a 30 g charge consisting of requisite proportions of iron and chromium or iron-chromium alloy was placed in the chromic oxide crucible in such a manner that the upper part would not touch the wall of the crucible and consequently, would drop down when the lower part was melted. This was to minimise the probability of arching of charge during the melting stage, and was achieved by breaking up the lump chromium into small pieces, mixing with iron and pressing into a pellet. In most of the experiments a high chromium Fe-Cr alloy was used to bring the charge (of a total weight of 30 g) to the desired chromium content. To avoid the reaction tube being splashed by the molten charge, the chromic oxide crucible was placed inside an alundum crucible of a larger diameter. The tube was then sealed off from the outside atmosphere and the current switched on to the furnace. In normal practice, the furnace was allowed to run on a small current overnight and in the morning the current was adjusted in such a way that the operating temperature could be attained in 4 - 5 hrs. Half an hour at 1700°C was found ample time to allow the charge to melt completely and also to get steady temperature conditions. Usually the melting was done in an atmosphere of argon except in very high chromium melts where it was thought preferable to melt under an atmosphere of argon and dryhydrogen mixture. The water bath temperature was also set

to give the required H_2O/H_2 ratio, and allowed to stabilise long before starting the experiment, preferably overnight. Argon was led through the saturating unit to flush off any entrapped air. After the charge had melted completely, hydrogen was allowed to pass through the saturators at a rate of 150 ml. per minute. The desired gas mixture was then bubbled gently through the molten charge by immersing the thin alumina tube (3 m.m.I.D.) into the melt to an approximate depth of 5 m.m. This was indicated by the small mercury manometer (M). By this bubbling technique apart from minimising thermal diffusion, equilibrium was achieved both by oxidation of Cr and reduction of Cr_2O_3. When the chromium content of the melt was in excess of that in equilibrium with the gas composition, some was oxidised till equilibrium was attained and when the chromium content of the melt was below the equilibrium content it was added to the melt by the reduction of the chromic oxide crucible. To establish each equilibrium point, a number of experiments were carried out for the same $\frac{H_2O}{H_2}$ ratio. This was especially the case when the $\frac{pH_2O}{pH_2}$ ration in the gas was low, since in these experiments the amount of oxygen which could be supplied to or taken from the oxide-metal system was very small and a fairly long experimental time was necessary to achieve a noticeable movement towards equilibrium. The duration of experiments under low $\frac{H_2O}{H_2}$ ratios was about 6 hrs. and thus the observed movement in either direction was found to be

significant. For higher $\frac{H_2O}{H_2}$ ratios the rate of oxidation or reduction was quite appreciable. During the experiment a constant check was made to see that the furnace temperature and the temperature of the water bath were steady, and that the gas mixture was bubbling through the melt uniformly. At the end of an experiment, the bubbling tube was raised out of the melt, the flow of hydrogen stopped and the furnace tube flushed with argon for about 5 minutes. The top bung was then removed and a sample of the metal taken by suction into a silica tube using a rubber bulb. Samples were quenched in water and were analysed for their chromium and oxygen contents. Only the middle portion of the sample was used for analysis and this was cleaned by filing.

Three experiments were made in which Fe-Cr-Ni alloys of known compositions were equilibrated with different $\frac{H_2O}{H_2}$ ratios. The charges (30 g) in these cases were brought to the desired chromium content by mixing high chromium Fe-Cr-Ni (10%) alloy with a Fe-Ni (10%) alloy. These alloys were prepared separately in recrystallised alumina crucibles by melting in an atmosphere of argon and hydrogen.

About half a dozen experiments were carried out to study the high temperature oxides of chromium. The controversial existence of the various oxides has already been discussed in detail in the previous chapter. In carrying out an experiment, chromium

powder and chromic oxide mixed in proportions corresponding to "CrO" were pelletted and placed in a molybdenum crucible. Alongside were placed an other pellet of pure Cr_2O_3 in the same crucible. This crucible was suspended into the furnace tube by means of a molybdenum wire. The top bung was provided with an arrangement to grip the wire in a gas tight joint and allowance made for the crucible to be pulled up easily in the cooler part of the tube after the experiment. The pellets were held at 1700°C for about 2 hrs. under an atmosphere of hydrogen/water vapour mixture. The oxygen potentials of these gaseous mixtures were kept low. At the end of the experiment the crucible was pulled up into the cooler part of the tube and the samples quenched in a strong current of argon. A more rapid quenching technique was also tried by droping the crucible along with the contents in a bucket of water placed underneath the furnace tube. The samples were studied by microscopic examination, X-ray diffraction analysis and the chemical analysis. These analytical techniques did not lead to any definite conclusions. These observations are discussed later.

In other trials, an effort was also made to study the volatile nature of any low oxides of chromium. The apparatus and technique employed resembled that used by Ramstad and Richardson[62] in their study of silicon monoxide. A horizontal platinum wound furnace attaining a maximum working temperature of 1550°C was used.

Hydrogen was passed over the chromic oxide placed in an alumina boat, followed by an alumina condenser tube placed in the cooler part of the furnace tube. No condensate was obtained in a 4 hr. duration.

(vi) ANALYSIS.

CHROMIUM.

This was analysed by persulphate oxidation method as described in the "Standard Methods of Analysis of Iron, Steel and Ferro Alloys"(63).

A known weight of the sample was dissolved in sulphuric-phosphoric acid mixture. When practically all action had ceased, a few drops of concentrated nitric acid were added and the solution was boiled for several minutes to expel oxides of nitrogen. The solution was then diluted to 300 ml. and boiled, adding a few small pieces of silica, followed by 25 ml. of a 10% silver nitrate solution containing traces of MnO_2 and about 2 gms. of ammonium persulphate to thoroughly oxidise the chromium and the liquid was boiled for at least five minutes. The pink colour due to MnO_2 appeared as soon as the chromium had been completely oxidised by the ammonium persulphate. Excess persulphate was removed by boiling and any MnO_4 was destroyed by the addition of about 15 ml. of 30% hydrochloric acid. The solution was allowed to cool to room temperature and an excess of 0.1 N ferrous ammonium solution was added from a burette. This reduces the chromium to the trivalent state as shown by the following equation:

$$2H^2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6H_2O$$

The excess of ferrous ammonium sulphate was titrated against 0.1 N potassium permanganate solution. The end point was a faint pink colour. Knowing the volume of 0.1 N ferrous ammonium sulphate required to reduce chromic acid, chromium was determined by the relation:

1 ml. of 0.1 N ferrous ammonium sulphate = 0.001734 gms. of Cr.

This method was found quite reliable as it gave concordant results on duplicate samples.

OXYGEN

Oxygen analyses of the metal samples were made by the vacuum fusion method on an apparatus which had been used in this department by Charlton[23] and McLean[59]. These workers[23, 59] had made some changes in the pumping and gas analysis side of this apparatus. A systematic diagram of the whole set split into two sections is shown in Figs. (9) and (10).

FURNACE OR REDUCTION CHAMBER.

This consisted of a silica tube which housed a graphite crucible assembly together with a mechanically operated graphite stopper working from an external electrical drive. The furnace tube was cooled by means of water circulation within a pyrex glass tube surrounding it. The glass tube was supported on a double deck sliding platform. The lower deck had an induction coil for heating the crucible. On the upper deck an electromagnet in the form of a horizontal wound solenoid was supported outside the glass tube.

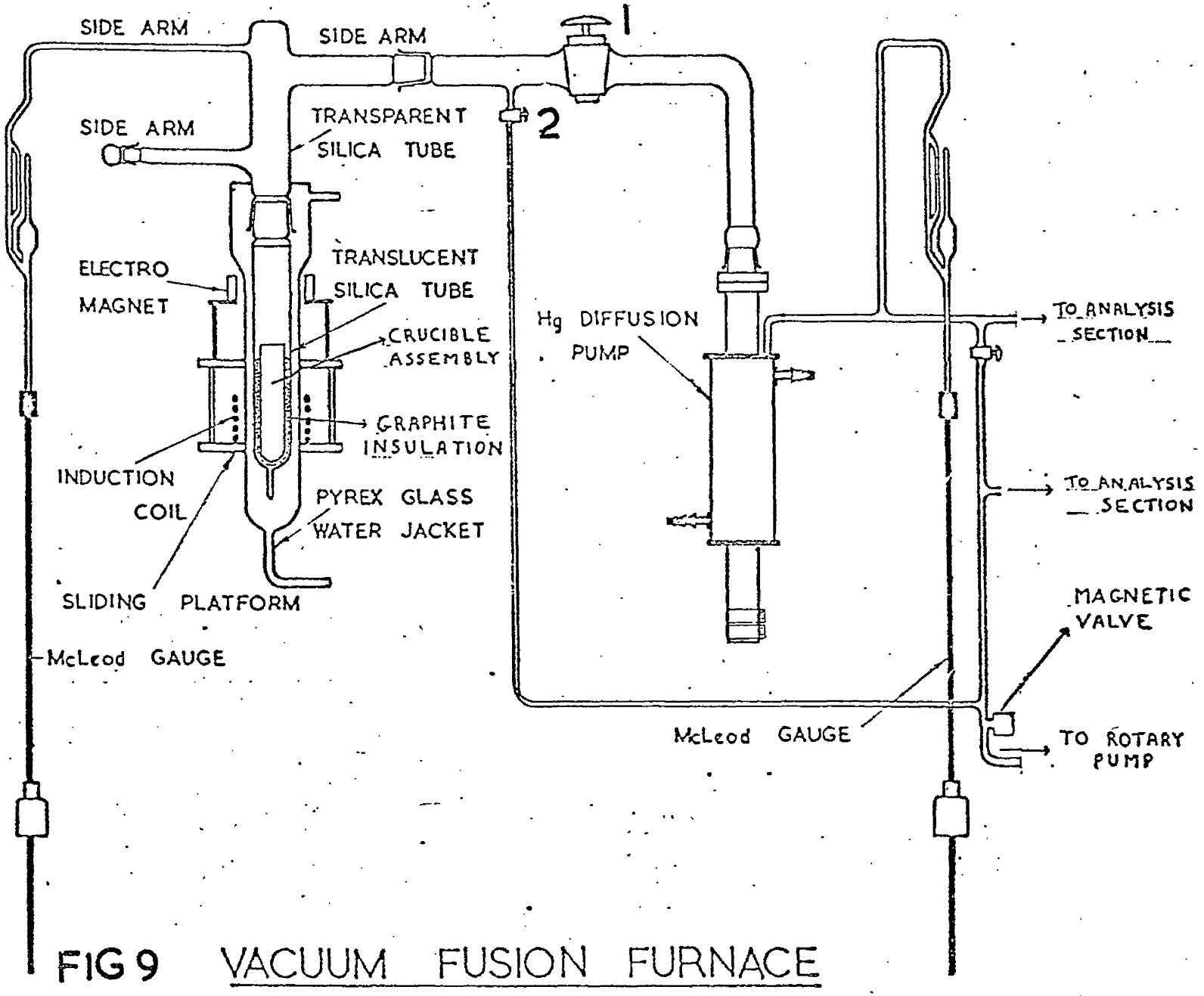


FIG 9 VACUUM FUSION FURNACE

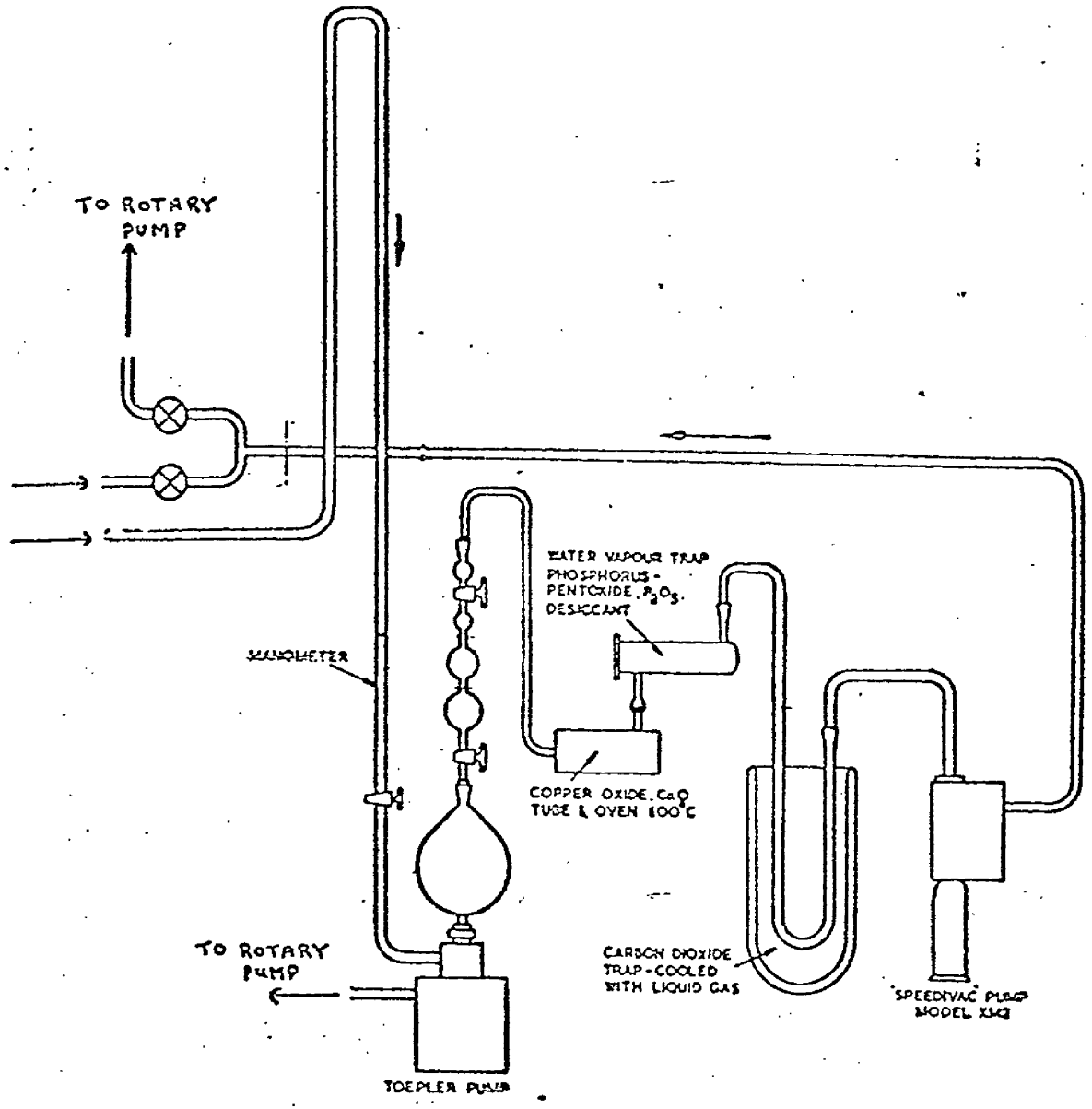


FIG 10 ANALYSIS SECTION

PUMPING EQUIPMENT.

The apparatus was evacuated using an Edwards "Speedivac" high vacuum pump type 1550 with integral P_2O_5 moisture trap backing on an Edwards Mercury diffusion pump type 2M4. Accidental flooding of the system with rotary pump oil was guarded against by the provision of an Edwards 1" air admittance magnetic valve at the rotary pump end of the backing line. The rotary pump could give a vacuum of 5×10^{-3} m.m. Hg. measured by an Edwards tilting type "vacustat." The Toepler pump as well as the furnace head McLeod gauge were operated by means of a Speedivac 15150 rotary pump.

GAS ANALYSIS SYSTEM.

This consisted of a necessary number of greased or waxed joints leading to the gas collection space, to the oxidation furnace and to the absorption traps, for the oxidised gases. The gas collection line was connected to the Toepler pump having an approximate volume of 1000 ccs. together with a series of calibrated bulbs giving total volumes of 1.26, 5.21, 20.66, and 51.76 ccs. A 90 cms. glass manometer was connected to the Toepler pump for measuring the pressure of gases. The furnace which was held at 400 - 450°C contained cupric oxide as an oxidising agent. This was prepared by heating copper powder in air. The trap for absorbing water vapours contained P_2O_5. The trap for freezing out carbon dioxide was cooled with liquid oxygen.

EXPERIMENTAL TECHNIQUE.

The vacuum fusion method depends fundamentally on the affinity of carbon for oxygen and its ability to decompose oxides at high temperatures and high vacuum with the formation of carbon monoxide.

(1) PREPARATION OF THE SAMPLE.

Samples weighing from 1 - 2 grms depending on the oxygen content were taken. They were cut from the metal samples with a hacksaw, and outer surface cleaned and rounded with a file. Any greasy matter sticking to the samples was removed with benzene and acetone. They were then dried, weighed and introduced into the side arm of upper transparent silica tube which was closed by a pyrex glass cap.

(2) PACKING OF THE FURNACE TUBE.

A high grade graphite crucible assembly was packed into the furnace tube using -200 mesh high grade graphite powder serving as thermal insulation to reduce heat loss by radiation. The graphite powder was packed between the crucible assembly and the furnace tube with a great care to get a uniform thickness all around and upto about $\frac{1}{2}$" from the top of the crucible assembly. The crucible was closed with spherical graphite lid provided with shallow grooves. A graphite rod with a piece of soft iron tube at the top was screwed to the lid. The soft iron tube enabled the lid to be lifted by an electromagnet to allow the sample to enter the crucible. The furnace tube was joined to the transparent silica

head with apiezon was 1-10.

(3) EVACUATION OF THE APPARATUS.

The evacuation of the whole apparatus was done in two steps. Firstly by closing taps 1 and 2 (in Fig.9), the diffusion pump and the analysis system were evacuated. The initial pump down being taken slowly to avoid "CuO" from the furnace being sucked into the system. This was done by gradual closing of the air inlet on the magnetic valve which at the start was fully opened. When a vacuum of 5×10^{-3}mm. Hg as measured by the vacustat was attained, the mercury diffusion pump, the copper oxide furnace and the small mercury diffusion pump (circulating pump) were switched on and the system degassed to get back a steady vacuum of 5×10^{-3}mm. Hg. This system was then sealed off from the atmosphere by closing the proper stop cocks. The rotary pump was closed and the air inlet on the magnetic valve opened completely. Tap 2 was opened and the reduction chamber evacuated slowly by gradual closing of the air inlet over a period of 30 minutes. To avoid fluffing of the graphite powder it was found that if the graphite crucible assembly and the graphite powder were dried at about 200°C overnight the system could be evacuated more quickly.

(4) DEGASSING PROCEDURE.

Initial degassing was done through tap 2 with tap 1 closed. This was observed to guard against the graphite powder getting into the diffusion pump in case of fluffing. To avoid fluffing

the crucible was heated slowly till it was red hot. The diffusion pump was then brought into operation and the stopcock 1 and 3 opened and stopcock 2 closed. The crucible was then heated quickly to about 2000°C. Much higher degassing temperatures created numerous other difficulties like:

(a) Development of hot spots due to sintering of graphite powder and thus losing its insulating properties.

(b) The formation of a graphite film on the sides of silica tube due to volatilisation of graphite from the hotter parts. Some graphite particles from this film dropped back into the hotter parts when the lid was lifted for dropping the sample. They evolved gas and could cause error in the results. Sometimes this volatilization of graphite caused welding of graphite lid to the mouth of crucible which could not be removed and the analysis had to be stopped.

In the present work degassing for 7 - 8 hours at 2000°C gave quite low blank at a working temperature of 1600°C.

The temperature of operation was very important, particularly as it must not be too high or too low. In the first place the temperature must be high enough to melt the iron bath and dissolve the sample. This enabled the absorbed carbon to react with the oxide. The temperature should be such that these reactions occur rapidly enough to extract the gaseous products in a

reasonable time. Too high a temperature causes the volatilisation of metal which condenses on the cooler parts of the furnace tube and may absorb some of the evolved gases. An operating temperature of 1600°C was found quite satisfactory.

The "blank" was determined by holding the temperature of the crucible at the operating temperature without a sample, and collecting the gas evolved during the given time, usually half an hour. The gas was then analysed as will be mentioned for the analysis of the samples. The volume of the blank at 1600°C was 0.15 - 0.2 cc.s/hr. Comparison of the vacuum fusion data with that from other apparatus [64] is shown in Table (3).

Laboratory	Degassing Temp. °C	Degassing Time hrs.	working Temp.	Blank c.c./hr
National Physical Lab.	2600	2-2½	1550-1600	.004
United Steel Co. Ltd.	2000	2	1650	0.3 - 0.4
Sheffield University	2100	3	1650	0.9
Firth Brown Research Ltd.	2100	2	1650	0.9 - 1
Present work	2000	5-7	1600	0.15 - 0.2

GAS EXTRACTION AND ANALYSIS PROCEDURE.

If the gases were released from the sample very rapidly, it could cause the metal to spatter, which gave erratic results. If the spattered particles of molten metal came in contact with the silica tube, reaction between the molten metal (containing dissolved carbon) and silica might result in the formation of carbon

monoxide giving high values for oxygen. On the other hand if the spattered particles solidified after falling on the graphite powder or before falling on the silica tube, the oxygen results would be low. The spattering was avoided by lowering the temperature to about 1300°C before dropping the samples. Another advantage of lowering the temperature was that the sample did not stick to the crucible assembly if it missed the crucible. The sample could then be dropped back into the crucible by lowering the electromagnet and adjusting it to a proper pull for the sample. The temperature was then raised gradually to 1600°C. About 4 gms. of armco iron were dropped into the crucible prior to dropping the samples. This served as a molten bath and gave good conditions for the reaction. The gas extraction from a sample was normally completed within 15 - 20 minutes.

The gases were then compressed to a known volume in the calibrated bulbs of the Toepler pump and its pressure read on the manometer. The various taps were then adjusted and the gases circulated through the system by the circulating diffusion pump. Carbon monoxide was oxidised to carbon dioxide and hydrogen to water vapour by copper oxide at about 450°C. The water was absorbed by the drying agent phosphorous pentoxide. The top valve of the Toepler pump was then closed and the remaining gas was collected in the calibrated bulbs and its pressure was measured at the same volume as before. By simple subtraction the partial

pressure of hydrogen was obtained.

The gas was once more allowed to circulate, and this time CO_2 was frozen out using liquid oxygen in the trap. This left only nitrogen which was collected in the Toepler pump and its pressure was measured as before. Subtraction gave the partial pressure of CO_2.

From the partial pressures, the volume and temperature of the gases, their volume at N.T.P. was calculated. The exact volume of the gases was obtained by substraction of the blank for the corresponding time.

The accuracy of the results was checked with standard samples of known oxygen contents which gave reproducible results. The results reported in the present work are the mean of two or more concordant results.

RESULTS

RESULTS

The analyses of the experiments made are shown in Table (4). Both the chromium and oxygen analyses were normally done in duplicate, but if the reproducibility was found to be poor, they were checked further. Chromium analyses are reported both as weight per cent and mole fraction. Oxygen analyses are all reported as weight per cent.

All the experiments were made in chromic oxide crucibles.

The water vapour-hydrogen gas mixture was bubbled through the melt in all the experiments.

Distilled water was used as a source of water vapour in case of $\frac{H_2O}{H_2}$ ration higher than 0.02. For low oxygen potentials, (i.e. $\frac{pH_2O}{pH_2}$ = 0.007 - 0.02), oxalic acid/oxalic acid dihydrate mixture was used as a source of water vapour.

TABLE 4.

Experimental results at 1700°C. Gas bubbled through the melts.

RUN NO.	CHROMIUM CHARGED		FINAL CHROMIUM		$\frac{pH_2O}{pH_2}$	%O
	wt.%	NCr	wt%	NCr		
1.	25.0	0.264	22.52	0.238	0.0136	-
2.	20.0	0.212	18.32	0.194	0.0193	-
3.	18.0	0.191	17.04	0.181	0.0193	-
4.	25.0	0.264	23.65	0.250	0.0169	-
5.	20.0	0.212	19.66	0.212	0.017	-
6.	24.0	0.254	22.82	0.242	0.014	-
7.	21.0	0.223	21.14	0.224	0.014	-
8.	25.0	0.264	23.3	0.246	0.0108	-
9.	23.0	0.243	23.16	0.245	0.0108	-
10.	30.0	0.316	28.08	0.296	0.0051	-
11.	28.0	0.295	27.2	0.287	0.005	-
18.	21.0	0.223	21.24	0.225	0.0165	0.0765
19.	18.0	0.191	20.04	0.215	0.02	0.0624
20.	25.0	0.264	25.2	0.266	0.0149	0.0635

TABLE 4 (CONT.)

RUN NO.	CHROMIUM CHARGED wt.%	CHROMIUM CHARGED NCr	FINAL CHROMIUM wt.%	FINAL CHROMIUM NCr	$\frac{pH_2O}{pH_2}$	ΔQ
21.	30.0	0.316	27.56	0.291	0.0105	-
22.	30.0	0.316	27.73	0.292	0.0107	-
23.	27.0	0.285	29.56	0.311	0.0106	0.1087
24.	31.0	0.326	30.28	0.319	0.0106	0.0859
25.	35.0	0.367	35.68	0.374	0.00539	-
26.	40.72	0.425	40.28	0.421	0.0072	0.194
27.	38.0	0.398	38.56	0.403	0.0071	0.1301
28.	23.0	0.243	23.16	0.245	0.0163	0.0888
29.	39.0	0.408	35.84	0.375	0.007	-
30.	39.0	0.408	34.64	0.363	0.007	-
31.	39.96	0.417	37.52	0.393	0.007	0.1150
32.	24.0	0.254	22.63	0.239	0.016	0.0994
33.	37.0	0.388	33.4	0.351	0.007	-
34.	39.0	0.408	38.26	0.400	0.007	0.0956
35.	20.0	0.212	20.64	0.219	0.0198	0.0956

TABLE 4 (CONT.)

RUN NO.	CHROMIUM CHARGED wt.%	CHROMIUM CHARGED NCr	FINAL CHROMIUM wt.%	FINAL CHROMIUM NCr	$\frac{pH_2O}{pH_2}$	$\frac{x}{O}$
36.	24.0	0.254	24.12	0.255	0.0164	0.114
37.	39.0	0.408	37.4	0.391	0.007	0.1852
38.	15.0	0.159	16.32	0.174	0.0266	0.0648
39.	18.0	0.191	18.72	0.199	0.0264	0.0659
40.	15.0	0.159	15.4	0.164	0.0323	0.0654
41.	13.0	0.139	14.0	0.149	0.0382	0.0751
42.	12.0	0.128	12.96	0.138	0.0521	0.0652
43.	31.0	0.326	30.76	0.324	0.0106	0.1339
44.	11.0	0.118	11.84	0.127	0.0777	0.0585
45.	13.0	0.139	11.8	0.126	0.0799	0.0719
46.	14.0	0.149	14.56	0.155	0.0527	0.0446
47.	16.0	0.17	15.76	0.168	0.0389	0.0676
48.	17.0	0.181	15.32	0.163	0.0316	0.0694

TABLE 4 (CONT.)

Experimental results at 1600°C. Gas bubbled through the melts.

RUN NO.	CHROMIUM CHARGED		FINAL CHROMIUM		$\frac{pH_2O}{pH_2}$	%O
	wt.%	NCr	wt.%	NCr		
12.	17.0	0.181	15.56	0.165	0.0149	-
13.	15.0	0.159	14.16	0.151	0.015	-
14.	21.0	0.223	15.87	0.168	0.0107	-
15(a)	16.0	0.17	14.16	0.151	0.0106	-
15(b)	16.0	0.17	14.76	0.156	0.0109	-
16(a)	13.0	0.139	11.16	0.119	0.0164	-
16(b)	13.0	0.139	12.24	0.13	0.0162	-
16(c)	13.0	0.139	13.26	0.14	0.0164	0.0516
17.	15.0	0.159	16.96	0.18	0.0147	0.0586

DISCUSSION

DISCUSSION

(1) CHROMIUM-OXYGEN EQUILIBRIA.

The oxygen analyses of various selected experiments at 1700°C are given in table (5). The results presented are the mean of two concordant values. Samples in the present work contained from about 0.05 to 0.19% oxygen and for these the reproducibility was ± 0.003%. If the reproducibility of the results was poor, the analysis was repeated and mean of the two close values taken. Not all the melts were analysed for their oxygen contents, because of the various complexities encountered in the oxygen analysis by vacuum fusion method. Therefore the oxygen analysis of the experiments which were considered far away from the equilibrium values are not reported.

Chromium analyses were also done in duplicate and normally agreed very closely. As the method used was a standard method there seemed to be little doubt about the validity of the results of these analyses. The average reproducibility was ±0.07%.

TABLE 5.

RUN NO.	Wt. % Chromium	$\frac{pH_2O}{pH_2}$	%Q
18.	21.24	0.0165	0.0765
19.	20.04	0.02	0.0624
20.	25.2	0.0149	0.0635
23.	29.56	0.0106	0.1087
24.	30.28	0.0106	0.0859
26.	40.28	0.0072	0.194
27.	38.56	0.0071	0.1301
28.	23.16	0.0163	0.0888
31.	37.52	0.007	0.1150
32.	22.63	0.016	0.0994
34.	38.26	0.007	0.1397
35.	20.64	0.0198	0.0956
36.	24.12	0.0164	0.114
37.	37.4	0.007	0.1852

TABLE 5 (CONT.)

RUN NO.	WT.%CHROMIUM	$\frac{pH_2O}{pH_2}$	$\frac{}{Q}$
38.	16.32	0.0266	0.0648
39.	18.72	0.0264	0.0859
40.	15.4	0.0323	0.0654
41.	14.0	0.0382	0.0751
42.	12.96	0.0521	0.0652
43.	30.76	0.0106	0.1339
44.	11.84	0.0777	0.0585
45.	11.80	0.0799	0.0719
46.	14.56	0.0527	0.0446
47.	15.76	0.0389	0.0876
48.	15.32	0.0316	0.0694

The equilibrium ratio for the reaction

$$H_2 + \underline{O} \rightleftharpoons H_2O \qquad \ldots\ldots\ldots\ldots (1)$$

can be written as

$$K'_1 = \frac{pH_2O}{pH_2 \times \% \underline{O}}$$

From the present results at 1700°C, the value of K'_1 can be calculated knowing the equilibrium $\frac{H_2O}{H_2}$ ratios and the oxygen concentrations corresponding to particular chromium concentrations, e.g. for

$$Cr = 21.24\%$$

$$\frac{pH_2O}{pH_2} = 0.0165$$

$$\% \underline{O} = 0.0765$$

$$K'_1 = \frac{0.0165}{0.0765} = 0.216$$

In the Fe-Cr-O system however $K'_1 = \frac{pH_2O}{pH_2 \times \% \underline{O}}$ is not a constant, but varies with chromium concentrations due to interaction effects. An extrapolation of the log K' v NCr plot to zero per cent chromium should give a value of K'_1 (i.e. K_1) relating to the equilibrium in iron. This extrapolated value of K' can then be compared with the accepted value of log K in Fe-O system to asses the reliability of the experimental data.

The equation for the equilibrium constant for the reaction:

$$H_2 + \underline{O} \qquad H_2O$$

in pure iron, by various data are given in table (5).

TABLE (5)

Comparison of K values for the reaction

$H_2 + \underline{O}$ H_2O (in Fe - O system)

	Presentation	Effect of temperature on the equilibrium constant.	log K values at 1700°C.
1)	V.V. Averin A.Y. Polyakow (14) & A.M. Samarin	$\log K = \frac{9,440}{T} - 4.536$	0.249
2)	N. A. Gokcen (6)	$\log K = \frac{6,670}{T} - 3.20$	0.18
3)	T.P. Floridis & J. Chipman (7)	$\log K = \frac{7,050}{T} - 3.20$	0.373
4)	K. Sano & H. Sakao (15)	$\log K = \frac{7,040}{T} - 3.224$	0.344
5)	S. Matoba & G. Gunji (13)	$\log K = \frac{7,540}{T} - 3.455$	0.367

The best values of the equilibrium constant for the reaction (1) in pure iron are considered to be that of Floridis and Chipman[7] and Sano and Sakao[15].

The present results at 1700°C have been plotted as log K v wt. per cent chromium in Fig (11). An extrapolation

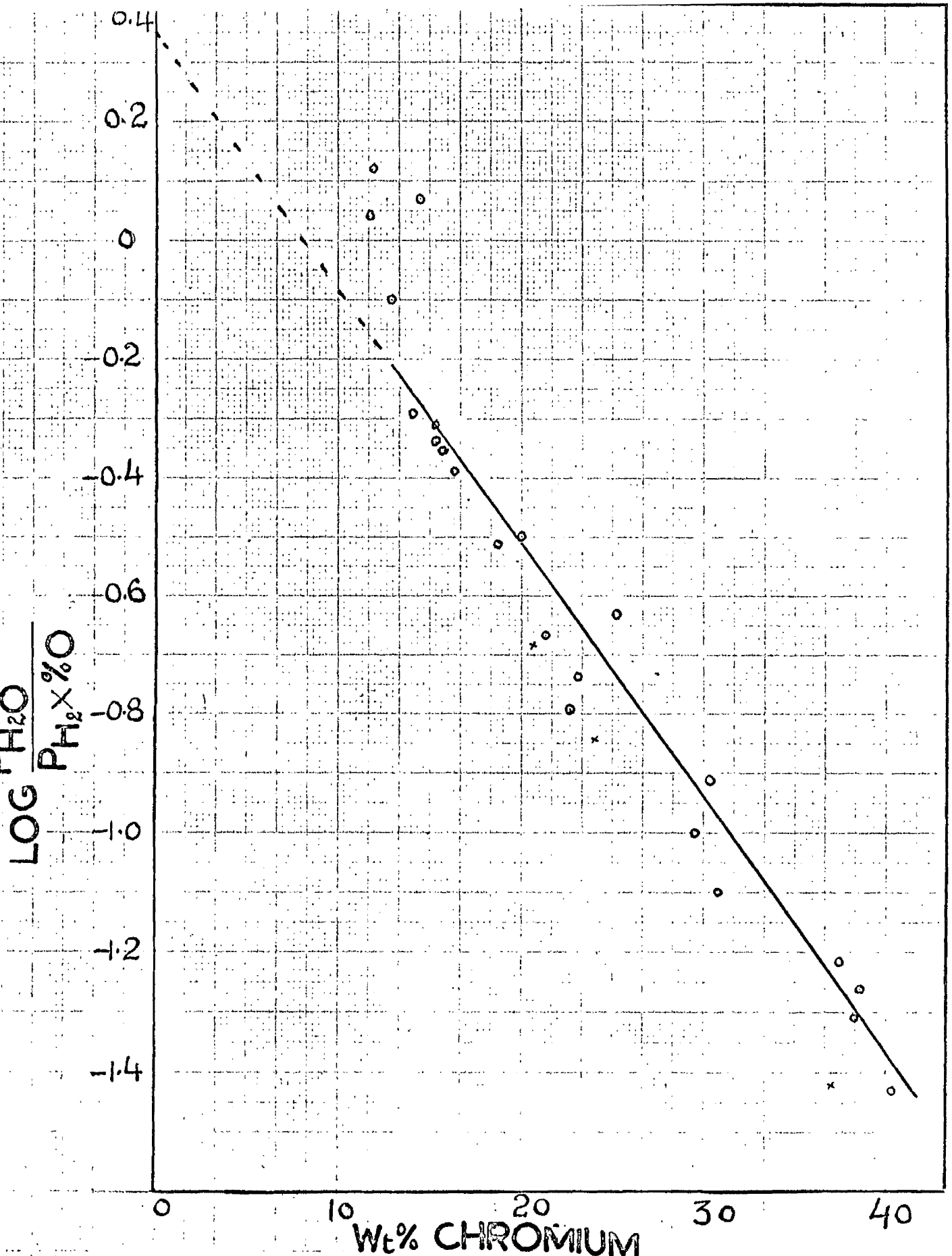


FIG 11 EXTRAPOLATION OF LOG $\frac{P_{H_2O}}{P_{H_2}\times\%O}$ BACK TO ZERO PERCENT CHROMIUM TO COMPARE WITH VALUES FOR PURE IRON

of the most representative line drawn through the present results, to zero per cent chromium gives a value of $\log K'_1 = 0.35$ This is in very good agreement with the accepted values of Floridis and Chipman[7] and Sano and Sakao[15]. Their [7, 15] values for log K at 1700°C are 0.37 and 0.34 respectively.

Since the interaction coefficients in the alloy system are calculated relative to the equilibrium data in pure iron, accurate data on the Fe-O system is essential. The results of Floridis and Chipman[7] and Sano and Sakao[15] have been obtained after the most careful considerations of the effects of thermal diffusion and the method of sampling, therefore their[7, 15] data should be reliable. The work of Chen and Chipman[20] and of Charlton[23] on equilibrium in the Fe-Cr-O system at 1600°C has emphasised the importance of accurate data on k_1 in order to determine the interaction effects in the melt. Their results[20,23] at 1600°C are shown with the present data at 1700°C in Fig (12) as log K' v wt.% chromium. Extrapolation of Charlton's[23] results to zero per cent chromium given a value of $\log K'_1 = 0.59$ which is in close agreement with Floridis and Chipman's[7] value for log K = 0.57 at 1600°C. Charlton[23] used Floridis and Chipman's[7] value in his calculations to determine the effect of chromium on the activity of oxygen in the alloys. On the other hand, extrapolation of Chen and Chipman's[20] results to zero per cent

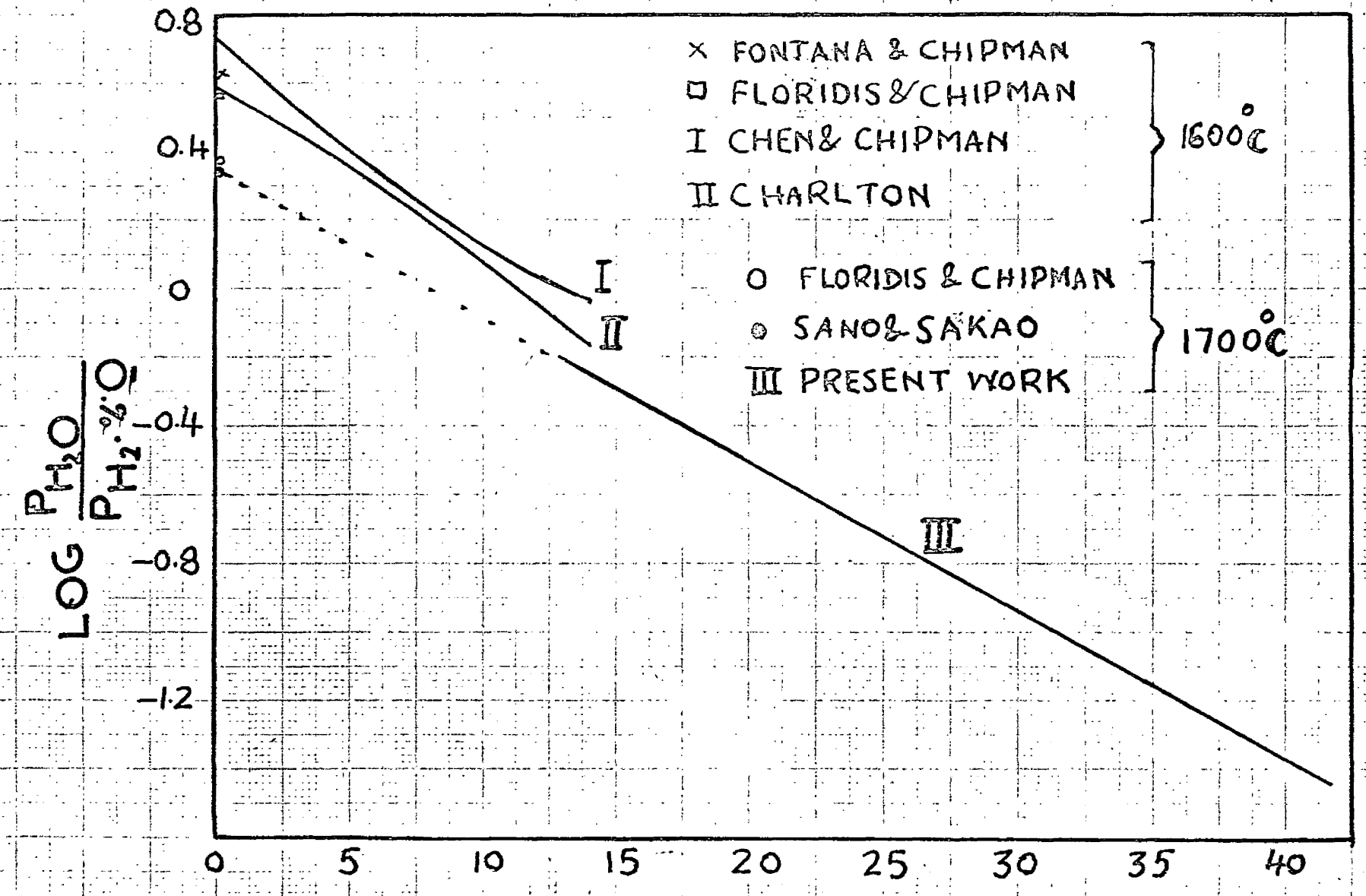


FIG 12 EXTRAPOLATION OF LOG $\frac{P_{H_2O}}{P_{H_2}\cdot\%O}$ BACK TO ZERO PER CENT CHROMIUM TO COMPARE WITH VALUES FOR PURE IRON

chromium gives a value of $\log K'_1 = 0.73$. This seems to be very high and could be attributed to the errors arising from thermal diffusion in their[20] experiments. Chen and Chipman[20] in their calculations used the value of Pontana and Chipman[3] for log K which has since been found to be in error due to thermal diffusion. Their[3] value for log K was 0.62 at 1600°C.

From the above considerations it can be said that the present results at 1700°C and Charlton's[23] data at 1600°C are more reliable than any of the previous investigations. Because it is particularly important in the observations of the equilibrium in this system to eliminate the thermal diffusion in the $H_2 - H_2O$ gas mixture and to ensure a correct value of the equilibrium oxygen content. Both in the present study and Charlton's[23] work care was taken to prevent thermal diffusion and to quench the samples as rapidly as possible. The experiments were carried out for much longer periods (4 - 6 hrs) to ensure the attainment of equilibrium and equilibrium was approached from both directions.

The equilibrium data is shown in Fig (13)where the percentage of oxygen in equilibrium with chromium in the molten iron at 1700°C is plotted. The range of chromium content studied was 12 - 40% Cr. Chromium concentrations are expressed as mole fractions as tabulated in Table (6). Since the atomic weight

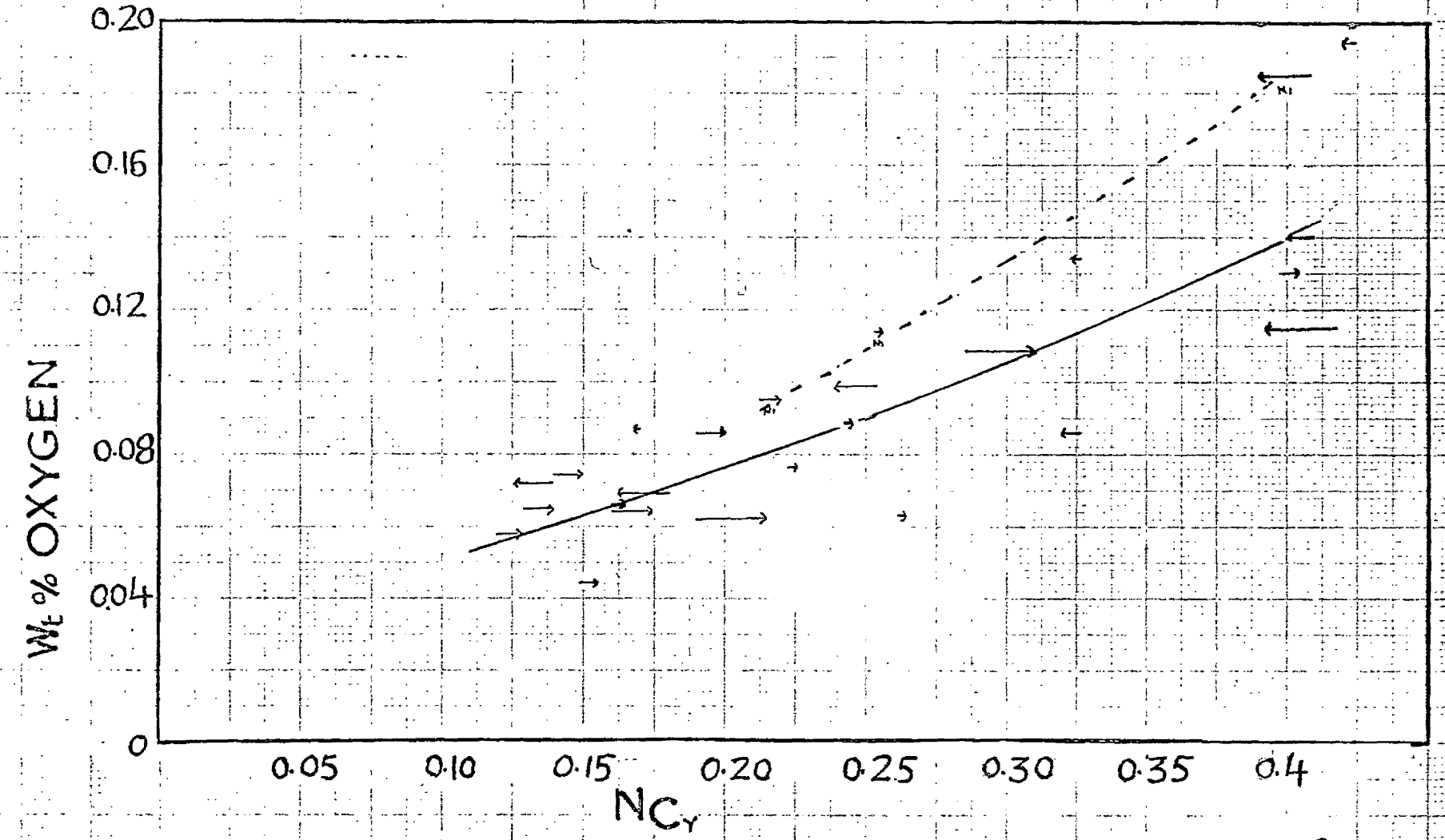


FIG 13 CHROMIUM – OXYGEN EQUILIBRIUM (1700°C)

of chromium and iron are similar, there is little difference in plotting mole fractions or weight per cents.

TABLE 6.

Run No.	NCr Initial	NCr Final	%O
18	0.223	0.225	0.0765
19	0.191	0.215	0.0624
20	0.264	0.266	0.0635
23	0.285	0.311	0.1087
24	0.326	0.319	0.0859
26	0.425	0.421	0.194
27	0.398	0.403	0.1301
28	0.243	0.245	0.0888
31	0.417	0.393	0.1150
32	0.254	0.239	0.0994
34	0.408	0.400	0.1397
35	0.212	0.219	0.0956
36	0.254	0.255	0.114
37	0.408	0.391	0.1852
38	0.159	0.174	0.0648
39	0.191	0.199	0.0859
40	0.159	0.164	0.0654
41	0.139	0.149	0.0751

TABLE 6 (CONT.)

Run No.	%Cr Initial	%Cr Final	%O
42	0.128	0.138	0.0652
43	0.326	0.324	0.1339
44	0.118	0.127	0.0585
45	0.139	0.126	0.0719
46	0.149	0.155	0.0446
47	0.17	0.168	0.0676
48	0.181	0.163	0.0694

Initial and final chromium concentrations are plotted to show the direction of observed movements towards the attainment of equilibrium. The scatter of the results is considered quite within the experimental errors. However, to draw a line which will be most representative of the experimental data, certain relevant facts have to be taken into consideration.

1. Primarily the direction of movement towards the equilibrium is considered most important.

2. Secondly lower oxygen results are considered to be more reliable. A vacuum fusion apparatus can give low results due to the absorption of evolved gases in the cooler parts of the furnace tube. This is quite negligible particularly when the oxygen content of the

metal is quite low and the pumping system is efficient. On the contrary, the results can be very high due to slight porosity or non metallic contamination of the metal samples.

From Fig. (13) it is quite significant that the oxygen content increases with increasing chromium concentrations in the range 12 - 40% chromium in Fe-Cr alloys. This has also been reported in the earlier studies on the Fe-Cr-O system. The results of various investigations at 1600°C are shown along with the present data at 1700°C in Fig (14). There has been no previous published data on the Fe-Cr-O system at 1700°C. Thus the comparision of the present data to that at 1600°C will only be a qualitative guide. However, apart from certain discrepancies, all these results show that additions of chromium first lower the solubility of oxygen in iron until a minimum is reached. Further additions of chromium increase the solubility of oxygen in iron. The nature of oxide phase precipitated is discussed later.

From Charlton's[23] results this limit for the minimum oxygen solubility has been shown at 7 - 7.5% chromium. Chen and Chipman's[20] data show this minimum at about 6% chromium. Chen and Chipman's[20] line shown in Fig (14) has been drawn through their experimental results rather than showing the extrapolated curve

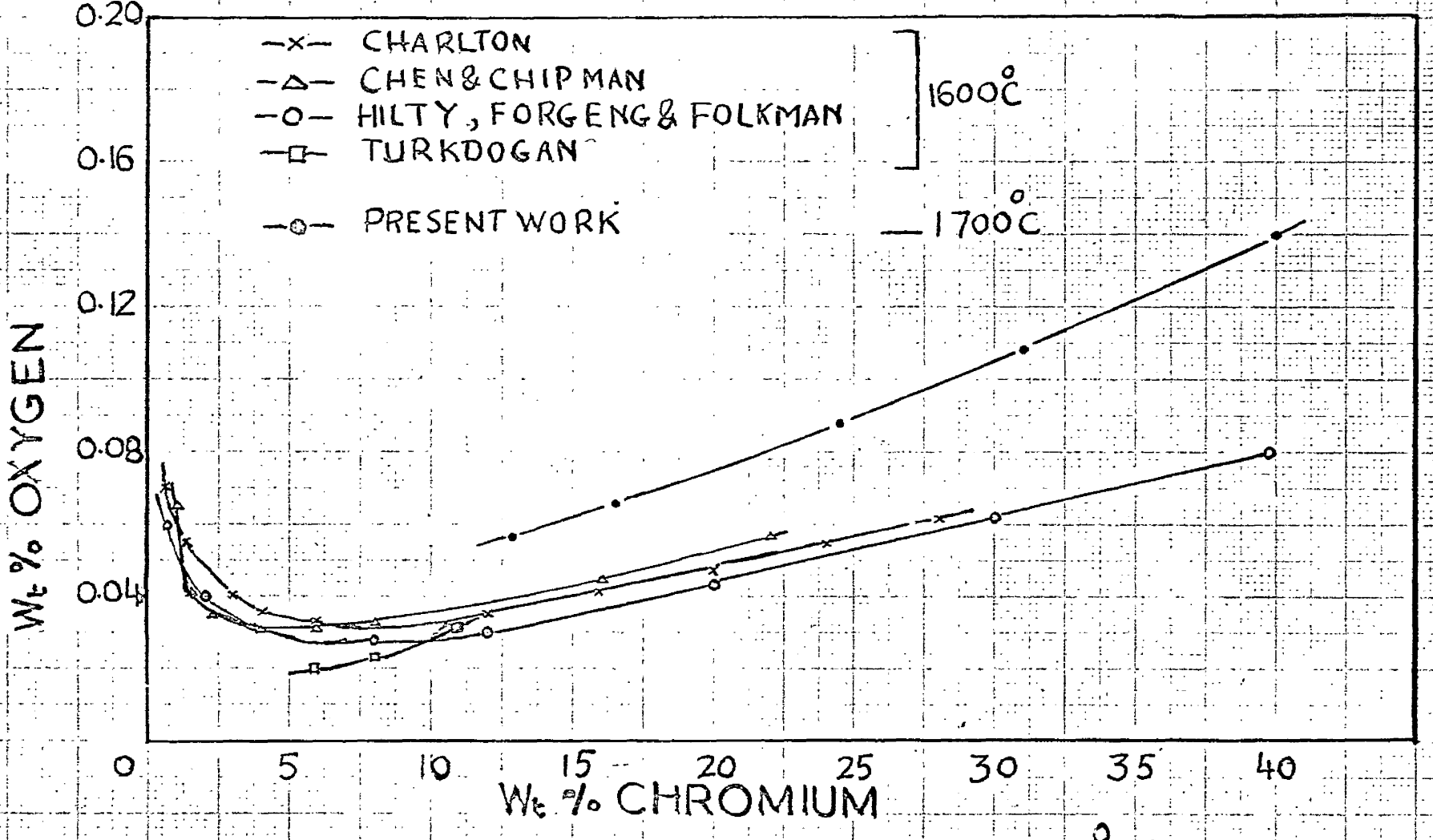


FIG 14 CHROMIUM–OXYGEN DATA (1700°C) & AVAILABLE DATA AT 1600°C

given in their paper. The results of Hilty, Forgeng and Folkman[30] show this minimum solubility limit from 5-10 per cent chromium. In this case[30] also the line was drawn to cover their lowest experimental values. In the original paper the line was shown much below their actual experimental oxygen results. Turkdogan's[32] few results in the range 4-12 per cent chromium do not show any minima.

In the present investigation the range of study (12 - 40% Cr) was above that which one might expect a minimum in the % Cr v %O plot at 1700°C.

However the significance of this minimum oxygen solubility corresponding to particular chromium concentrations implies that in low chromium alloys, chromium acts as a deoxidiser as well as an alloying element, while in high chromium alloys, chromium has virtually no deoxidising effects. This may have special importance with regard to the deoxidation and inclusion problems in high chromium steels. The solubility of oxygen in iron-chromium alloys is limited by the precipitation of certain oxide-phases corresponding to varying chromium concentrations. It has been postulated from the various data[20,23,30] on the Fe-Cr-O system that there is a gradual change in the oxide phases in equilibrium with chromium in the iron-chromium alloys, the trend is towards the formation of lower oxides of chromium

with increasing chromium concentrations. Although there is no unanimity about the exact oxide phases in equilibrium with chromium at high chromium concentrations, yet one thing is quite certain, that there is a gradual increase in the oxygen contents of iron-chromium alloys with increasing chromium concentrations beyond the minimum. (discussed earlier).

The presence of nickel in the iron-chromium alloys was found to further increase the oxygen solubility and thus lowers its activity co-efficient by a further amount. The dotted line shown in figure (13) represents the results with nickel. The effect of nickel cannot be considered in detail because only three experiments have been made in Fe-Cr-Ni-O system.

By comparing the equilibrium data on the reaction:

$$H_2 + \underline{O} \rightleftharpoons H_2O$$

in pure iron and iron-chromium alloys, the interaction coefficient f_O^{Cr}, can be calculated. This does not involve any assumptions regarding the oxide phases in equilibrium with the melts.

In the present work the value for K_1 given by Floridis and Chipman[7] has been used for the calculation of f_O^{Cr} as follows:

The equilibrium constant for the reaction:

$$H_2 + \underline{O} \rightleftharpoons H_2O$$

$$K'_1 = \frac{pH_2O}{pH_2 \times \%O} \quad \text{(in Fe-O and Fe-Cr-O system)}$$

$$K_1 = \frac{pH_2O}{pH_2 \times a_O}$$

$$= \frac{pH_2O}{pH_2 \times f_O \times \%O}$$

$$\log K = \frac{pH_2O}{pH_2 \times \%O} - \log f_O$$

$$\log K = \text{Log } K'_1 - \log f_O$$

$$\log f_O^{Cr} = \log K'_1 - \log K$$

Here K'_1 is the equilibrium constant for the reaction (1) in Fe-Cr-O system and K_1 is the equilibrium constant for the Fe-O system. The value of $\log K = 0.37$ at 1700°C is taken from Floridis and Chipman's[7] results. The value of $\log K'$ in turn can be calculated as shown previously.

e.g. for

$$NCr = 0.225$$

$$\frac{pH_2O}{pH_2} = 0.0165$$

$$\%O = 0.0765$$

$$K' = \frac{0.0165}{0.0765} = 0.216$$

Then:

$$\log f_O^{Cr} = \log 0.216 - 0.37$$

$$\log f_O^{Cr} = -1.0355$$

$$f_O^{Cr} = 0.09215$$

The data on f_O^{Cr} are presented in Table 7.

TABLE 7

Run No.	Wt.% Cr	NCr	f_O^{Cr}
18	21.24	0.225	0.092
19	20.04	0.215	0.137
20	25.3	0.266	0.100
23	29.56	0.311	0.042
24	30.28	0.319	0.052
26	40.28	0.421	0.016
27	38.56	0.402	0.023
28	23.16	0.245	0.078
31	37.52	0.393	0.026
32	22.63	0.239	0.069
34	38.26	0.400	0.021
35	20.64	0.219	0.088

TABLE (7) CONT.

Run No.	Wt.% Cr	NCr	γ_O^{Cr}
36.	24.12	0.255	0.061
37.	37.4	0.391	0.016
38.	16.32	0.174	0.17
39.	18.72	0.199	0.13
40.	15.4	0.164	0.21
41.	14.0	0.149	0.22
42.	12.96	0.138	0.34
43.	30.76	0.324	0.034
44.	11.84	0.127	0.57
45.	11.8	0.126	0.47
46.	14.56	0.155	0.50
47.	15.76	0.168	0.19
48.	15.32	0.163	0.19

The results are shown in Fig. (15) where γ_O^{Cr} is plotted against NCr. In the range 0 - 14 weight per cent chromium no experiments have been made and the dotted line shown in the graph is an extrapolation from the high chromium data. The method of calculation of the activity coefficient is based on the assumption

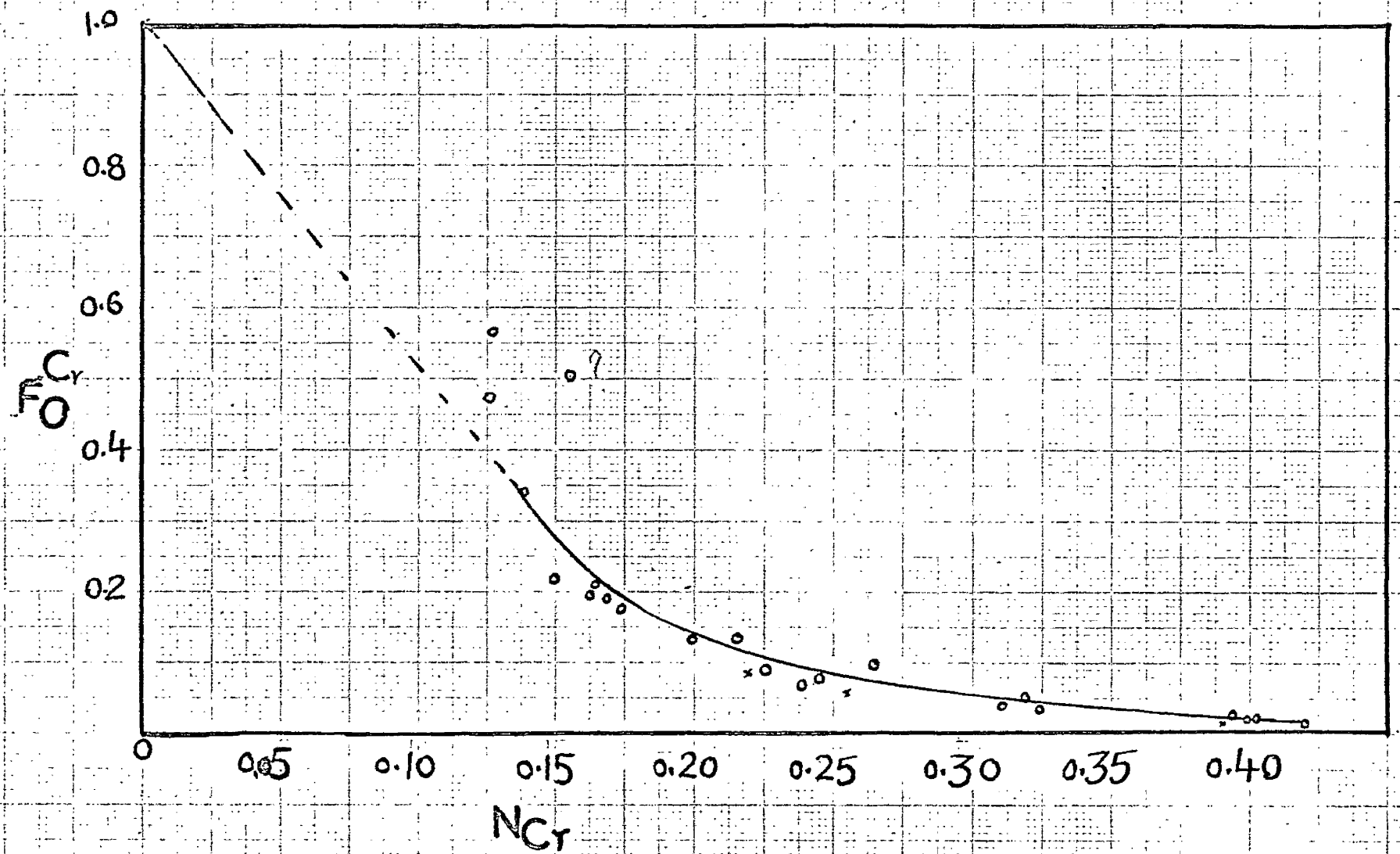


FIG 15 THE EFFECT OF CHROMIUM ON THE ACTIVITY-COEFFICIENT OF OXYGEN IN IRON AT 1700°C

that gas metal equilibrium has been attained. Therefore, in drawing the curve, the experimental points which lie on or are very near to the original $\frac{pH_2O}{pH_2}$ v %Cr curve are considered more important. Also it can be seen from the graph that all the experimental data isquite well served by the curve drawn, except three points at higher oxygen potentials. The deviation, particularly of one of these points corresponding to Run No. 46 is quite pronounced from the rest of the data. This can only be explained if it is considered that some of the oxygen might have escaped due to lowering of temperature before taking the sample. The reason being that at about the end of this run, the current failed and the time gap before a sample could be taken had considerably lowered the temperature of the melt, thus resulting in a possible loss of some of the equilibrium oxygen content. This consequently gave a much higher value of activity coefficient of oxygen.

In Fig. (16) $\log f_O^{Cr}$ has been plotted against wt.% chromium. All the relevant experimental results are shown and the best representative line is drawn. To obtain a value of the interaction parameter, Wagner's (47) relation:

$$e_O^{Cr} = \frac{\partial \log f_O^{Cr}}{\partial \% Cr}$$

is used.

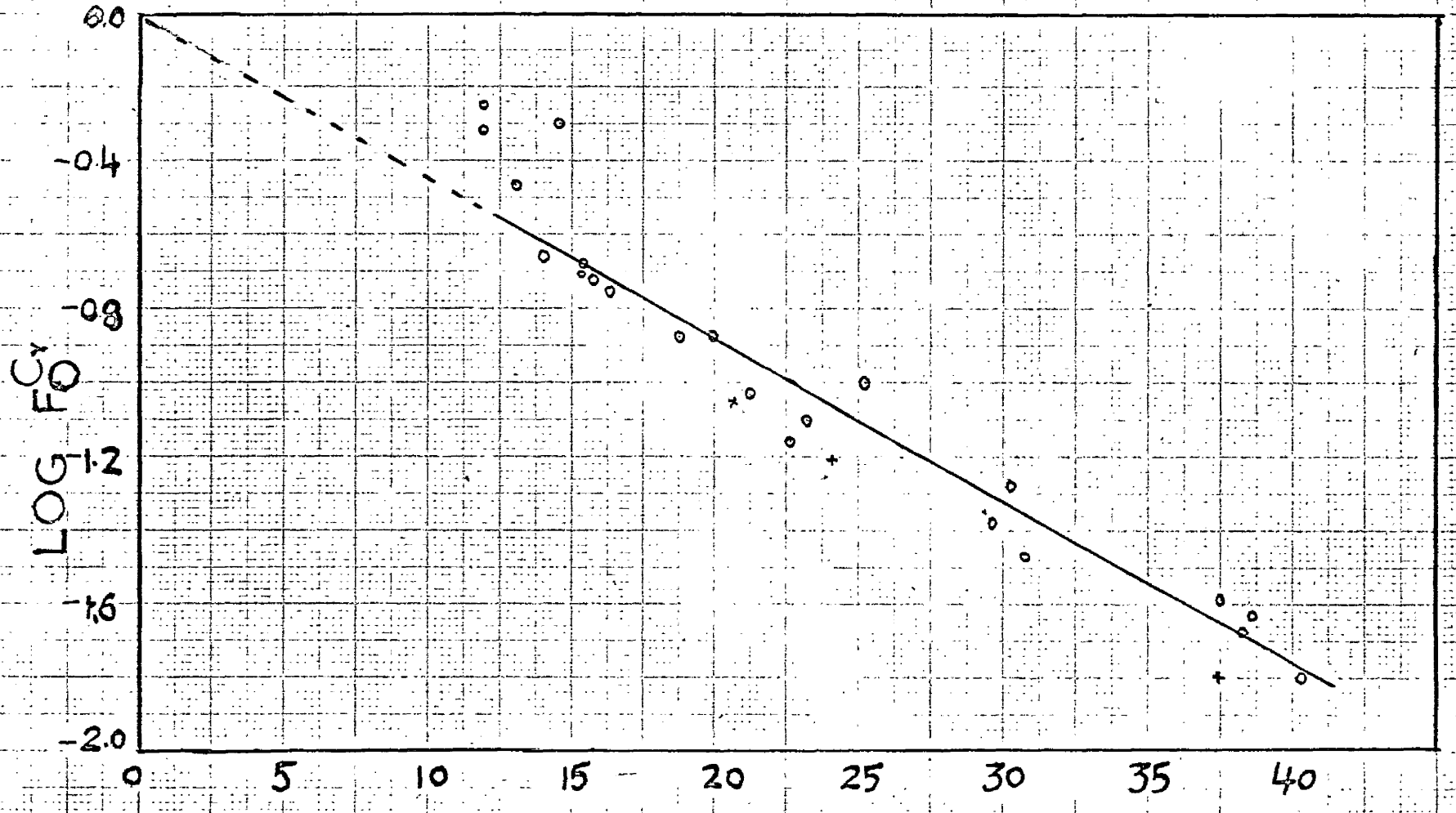


FIG16— THE EFFECT OF CHROMIUM ON THE ACTIVITY-COEFFICIENT OF OXYGEN IN IRON AT 1700°C

In the range of present investigations (14 - 40% Cr) a linear relationship holds and the interaction parameter found for this range is $\varepsilon_O^{Cr} = -0.044$.

This is shown again in Fig. (17) along with Charlton's [23] data at 1600°C. It can be seen from the graph that Charlton's[23] data shows a linear relationship in the range 0 - 14% chromium. Therefore, the value of interaction parameter $\varepsilon_O^{Cr} = -0.058$ is quoted for this range only. The values of interaction parameters as obtained from the various data are given in Table 8.

TABLE 8.

Presentation	Temperature °C	ε_O^{Cr}
Present work	1700	-0.044
Charlton[23]	1600	-0.058
Chen & Chipman[20]	1600	-0.041 (extrapolated values)
Chen & Chipman[20]	1600	-0.055 (experimental results)
Turkdogan[32]	1600	-0.064

It has been suggested that the parameters ε_O^M for the ternary system Fe-M-O decrease with increasing stability of the oxide of the metal M. As the stability of chromium oxide

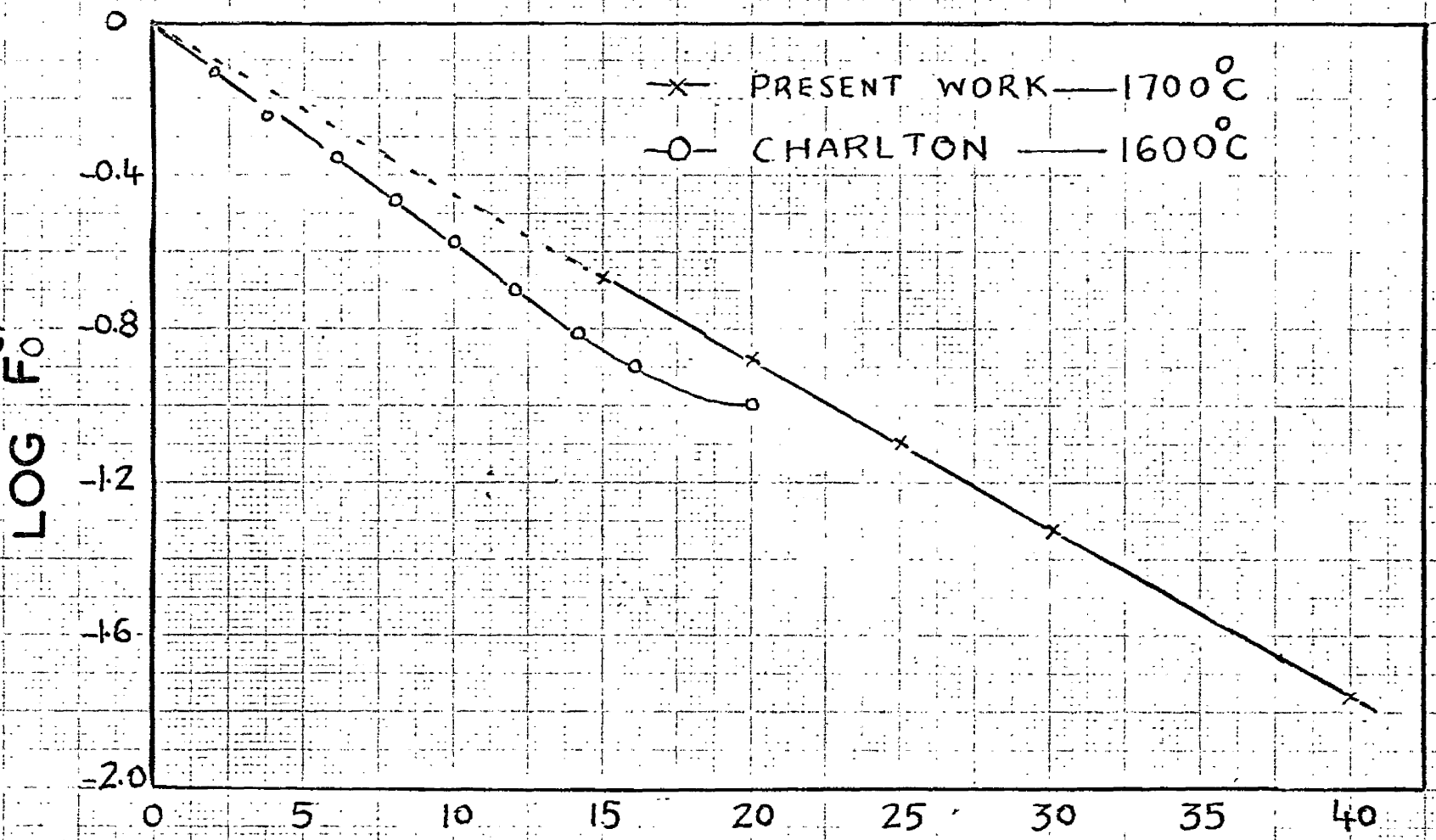


FIG 17 EFFECT OF CHROMIUM ON THE ACTIVITY-COEFFICIENT OF OXYGEN IN IRON.

decreases with increasing temperature, therefore e_O^{Cr} will increase with an increase in temperature. Under these considerations it can be concluded that the present value of e_O^{Cr} at 1700°C is in line with that of Charlton[23] at 1600°C.

Wagner[47] has shown that the following simple relation exists between the interaction parameters of two solutes in the same solvent i.e.

$$e_j^i = e_i^j$$

This relationship holds true only for dilute solutions and may not be applicable in the present work. Moreover in view of the relatively low concentrations of oxygen as compared with chromium in liquid iron, the value of ℓ_{Cr}^O is not significant.

When concentrations are expressed as mole fractions, the interaction parameters are quoted as:

$$\varepsilon_O^{Cr} = \frac{\partial \log f_O^{Cr}}{\partial N Cr}$$

From the present data it is found that:

$$\varepsilon_O^{Cr} = -4.4$$

In terms of interatomic attraction the negative values may be understood on the basis of a very simple model, illustrated

by the Fe-Cr-O solutions. In Fe-O- solutions each O atom is surrounded on the average by n Fe atoms which share the Fe-O bonding energy. The Cr-O bonding is stronger than the Fe-O bonding, and this leads to two results:

(1) The ratio Cr/Fe is greater amongst the nearest neighbours of O than in the bulk of the solution.

(2) The O atoms become more firmly bonded as the chromium concentration increases.

The model indicated above takes no account of the intermetallic bonding i.e. Fe-Cr which are probably very small.

From the present experimental observation on the chemical behaviour of chromium with respect to its reactions with oxygen in liquid iron at 1700°C it is concluded that:

In the Fe-Cr alloys for a given $\frac{H_2O}{H_2}$ ratio, the oxygen content increases with increasing chromium contents. This signifies that chromium lowers the activity coefficient of oxygen. To visualise the reason for large effect of chromium on the activity coefficient of oxygen, it may be supposed that oxygen atoms in the melt are more strongly bonded to chromium than to iron. The ratio of number of chromium-oxygen bonds to the number of iron-oxygen bonds is greater than the ratio of chromium to iron. This does not require that there be molecules of CrO and FeO in the melt although the presence of such oxides would be expected to lead to about the same results.

(ii) PHASE EQUILIBRIUM AND CHROMIUM ACTIVITY.

In presenting equilibrium data most of the earlier experiments(runs nos. 1 - 17) have been ignored. These were preliminary experiments, carried out to find the approximate equilibrium values corresponding to particular hydrogen-water vapour gas mixtures. From these results it was observed that the chromium concentrations were lower than the estimated values from the available data at 1600°C. Thus to check the functioning of the apparatus and the technique a few runs (13 - 17) were made at 1600°C for a direct comparison with the available data. This also indicated that the results were lower than those reported in the literature[23]. Later on it was noticed that the electrolytic iron being used in these experiments contained some brownish oxide particles. Therefore, in the subsequent experiments the iron used was pre-melted in an atmosphere of hydrogen to remove any traces of oxide present. Also from and including run 16 (c) onwards, a high chromium master alloy was used instead of virgin metals.

Equilibrium was normally approached from both the high chromium and the low chromium sides. To ensure that the value finally attained represented the true equilibrium state, several experiments were repeated for the same H_2O/H_2 ratios. All the

experimental results are shown in Table 4.

Fig. (15) shows the relationship between chromium contents of molten iron and equilibrium ration of water vapour to hydrogen. Chromium contents are expressed as mole fractions. Initial and final chromium contents are plotted to show the direction of observed movement. The arrow head indicates the final analysed chromium concentrations.

The curve drawn fits the experimental data well. All the points are served by this curve except a few points at high oxygen potential, but these can also be considered within the experimental error.

According to the phase rule the Fe-Cr-H_2O-H_2 system which consists of four components, iron, chromium, oxygen and hydrogen, has three degrees of freedom; the temperature, the pressure and the composition of the gas phase so that only three phases could be present in equilibrium with one another. Now that there was already a gas phase and a liquid phase (metal), only one solid oxide phase (or liquid phase) could exist under equilibrium conditions. When a solid phase in this case, crucible material was introduced into the system, it might remain as such if it were the stable solid phase under those conditions, or it might be dissolved continuously by the molten metal with the precipitation

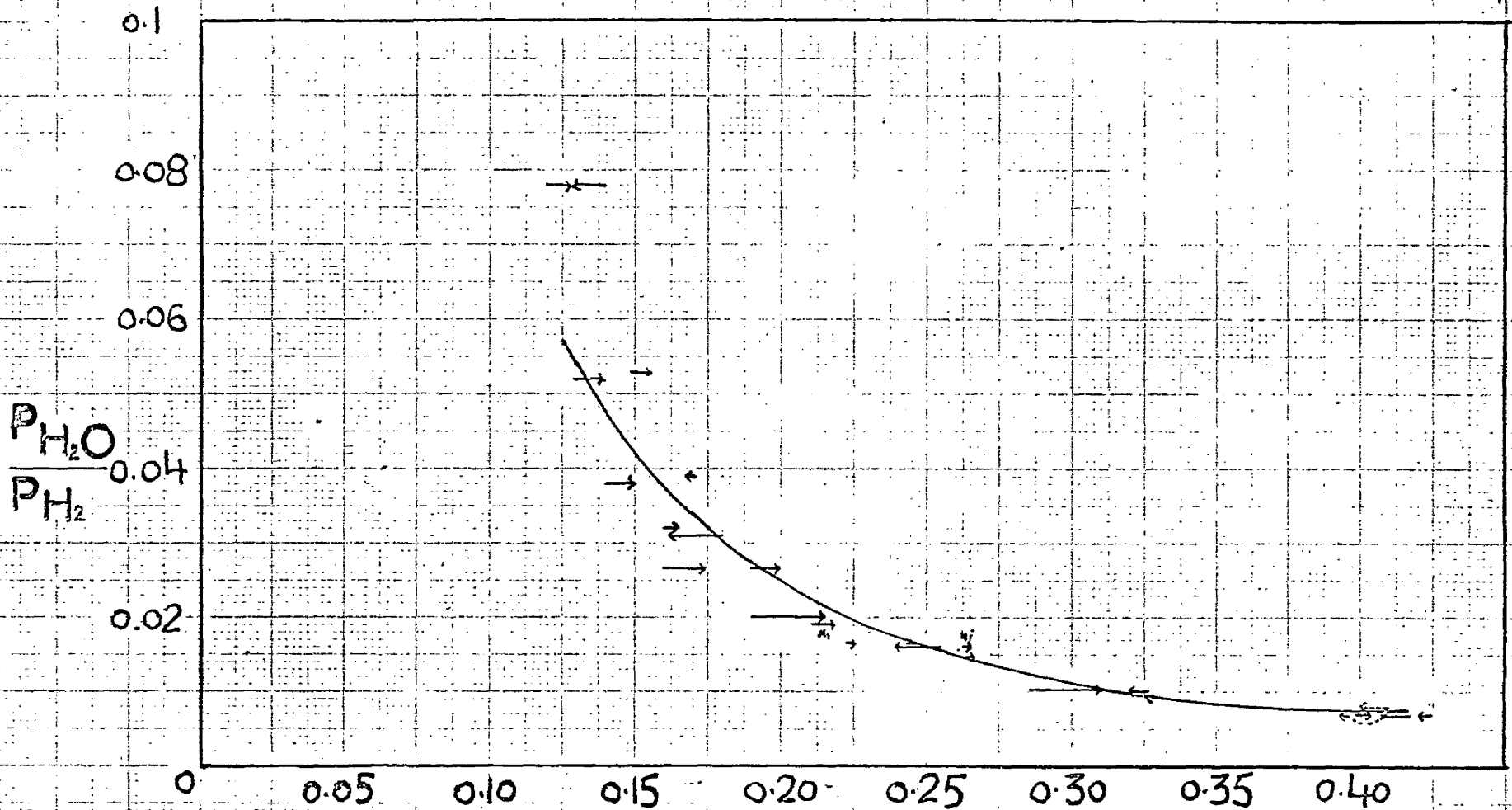


FIG 18 EFFECT OF $\frac{P_{H_2O}}{P_{H_2}}$ ON N_{C_V} AT 1700°C

of a new oxide phase from the metal, also continuously. This reaction would continue until one of the oxide phases disappeared.

In the present work the chromium concentration studied ranged from 12 - 40% chromium. If chromic oxide was the stable solid phase, then Cr - Cr_2O_3-gas equilibria will serve the experimental results. The reaction and equilibrium constant for this reaction are:

$$Cr_2O_3(s) + 3H_2(g) \rightleftharpoons 3H_2O\ (g) + 2Cr$$

$$K = \left\{ \frac{pH_2O}{pH_2} \right\}^3 \cdot (a_{Cr})^2$$

The free energy for the above reaction was calculated as follows:

From the thermaldata available on the standard Gibbs free energy of formation equation for Cr_2O_3,

$$2\ Cr\ (s) + \frac{3}{2}\ O_2 \rightleftharpoons Cr_2O_3\ (s)$$

$$\Delta G^0_1 = -274,750 - 6.11T \ln T + 2.01 \times 10^{-3}T^2 + 0.69 \times 10^5 T^{-1} + 105.95T \text{ cals}^{(65)}$$

and H_2O,

$$H_2 + \tfrac{1}{2}\ O_2 \rightleftharpoons H_2O$$

$$\Delta G^0_2 = -56,940 + 2.91\ T \ln T - 0.64 \times 10^{-3}\ T^2 - 0.08 \times 10^5\ T^{-1} - 8.11\ T \text{ cals}^{(65)}$$

The free energy of formation for the reaction:

$$Cr_2O_3(s) + 3H_2 \rightleftharpoons 3H_2O + 2\ Cr\ (s)$$

is calculated from the above equation as:

$$\Delta G^o_3 = 3\ \Delta G^o_2 - \Delta G^o_1$$

$$G^o_{1700} = 53,716 \text{ cals.}$$

From this the value of equilibrium constant is obtained using the relation:

$$\Delta G = -RT \ln K$$

$$= -4.575\ T \log K$$

$$\log K = -\frac{53,716}{4.575 \times 1973}$$

$$= -5.951$$

$$K = 1.12 \times 10^{-6}$$

Thus knowing the value of "K" the chromium activities corresponding to different H_2O/H_2 ratios are calculated from the relation:

$$K = \left\{ \frac{pH_2O}{pH_2} \right\}^3 \cdot (a_{Cr})^2$$

TABLE 9

Wt.% Cr	NCr	$\frac{pH_2O}{pH_2}$	a_{Cr} (s)	γ_{Cr} (s)	a_{Cr} (l)	γ_{Cr} (l)
21.24	0.225	0.0165	0.50	2.22	0.44	1.97
20.04	0.215	0.02	0.37	1.74	0.37	1.74
25.2	0.266	0.0149	0.58	2.19	0.52	1.94
29.56	0.311	0.0106	0.97	3.12	0.86	2.76
30.28	0.319	0.0106	0.97	3.04	0.86	2.70
40.28	0.421	0.0072	1.81	4.29	1.60	3.81
38.56	0.403	0.0071	1.81	4.48	1.60	3.98
23.16	0.245	0.0163	0.51	2.08	0.45	1.84
37.52	0.393	0.007	1.81	4.60	1.60	4.08
22.63	0.239	0.016	0.52	2.19	0.46	1.94
38.26	0.40	0.007	1.81	4.52	1.60	4.01
20.64	0.219	0.0198	0.38	1.73	0.34	1.54
24.12	0.255	0.0164	0.50	1.98	0.45	1.75
37.4	0.391	0.007	1.81	4.62	1.60	4.10
16.32	0.174	0.0266	0.24	1.40	0.22	1.25
18.72	0.199	0.0264	0.25	1.24	0.22	1.10
15.4	0.164	0.0323	0.18	1.11	0.16	0.99
14.0	0.149	0.0382	0.14	0.95	0.13	0.89
12.96	0.138	0.0521	0.09	0.64	0.08	0.57

TABLE 9 (CONT.)

Wt.% Cr	NCr	$\frac{pH_2O}{pH_2}$	a_{Cr} (s)	γ_{Cr} (s)	a_{Cr} (l)	γ_{Cr} (l)
30.76	0.32	0.0106	0.97	2.99	0.86	2.65
11.84	0.127	0.0777	0.05	0.39	0.04	0.35
11.8	0.126	0.0799	0.05	0.37	0.04	0.33
14.56	0.155	0.0527	0.09	0.57	0.08	0.50
15.76	0.168	0.0389	0.14	0.82	0.12	0.73
15.32	0.163	0.0316	0.19	1.15	0.17	1.02

The values of activities calculated as above are given in Table 9. These activities refer to pure solid chromium as the standard state. These values are converted to pure liquid chromium as the standard state using the relation:

$$\log a_l = \frac{\Delta H_f}{4.575}\left\{\frac{1}{T_m} - \frac{1}{T}\right\} + \log a_s$$

where a_l = activity of chromium relative to pure liquid.

a_s = activity of chromium relative to pure solid.

T = temperature of reaction in ^oK.

= 1700 + 273 = 1973^oK

and for chromium:

ΔH_f = 5,000 cals. (Kelley)

T_m = melting point of pure chromium = 1903 + 273 = 2176^oK.

The activities relative to pure liquid chromium as the standard state are also given in Table (9).

If these data are correct Fe-Cr alloys saturated with chromium should have been obtained in the experiments corresponding to $pH_2O/pH_2 < 0.01$, since in these experiments the calculated chromium activities correspond to a value of more than unity. The experimental equilibrium concentrations of chromium are much less than saturation and unless the data for the free energy of formation of Cr_2O_3 is in considerable error, the equilibrium being studied cannot be that between Cr_2O_3, Cr in liquid iron and $H_2 - H_2O$ gas.

To illustrate the validity of the reaction:

$$Cr_2O_3 + 3H_2 \rightleftharpoons 3H_2O + 2\underline{Cr}$$

and equation:

$$K = \left\{ \frac{pH_2O}{pH_2} \right\}^3 \cdot (a_{Cr})^2$$

$\log \frac{pH_2O}{pH_2}$ is plotted against log NCr in Fig (19). Such a graph should give a straight line having a slope of -2/3 in the chromium range studied if chromic oxide is the stable oxide phase in equilibrium with the metal and solutions of chromium in iron obey Raoult's Law. This would justify the assumptions made in deriving

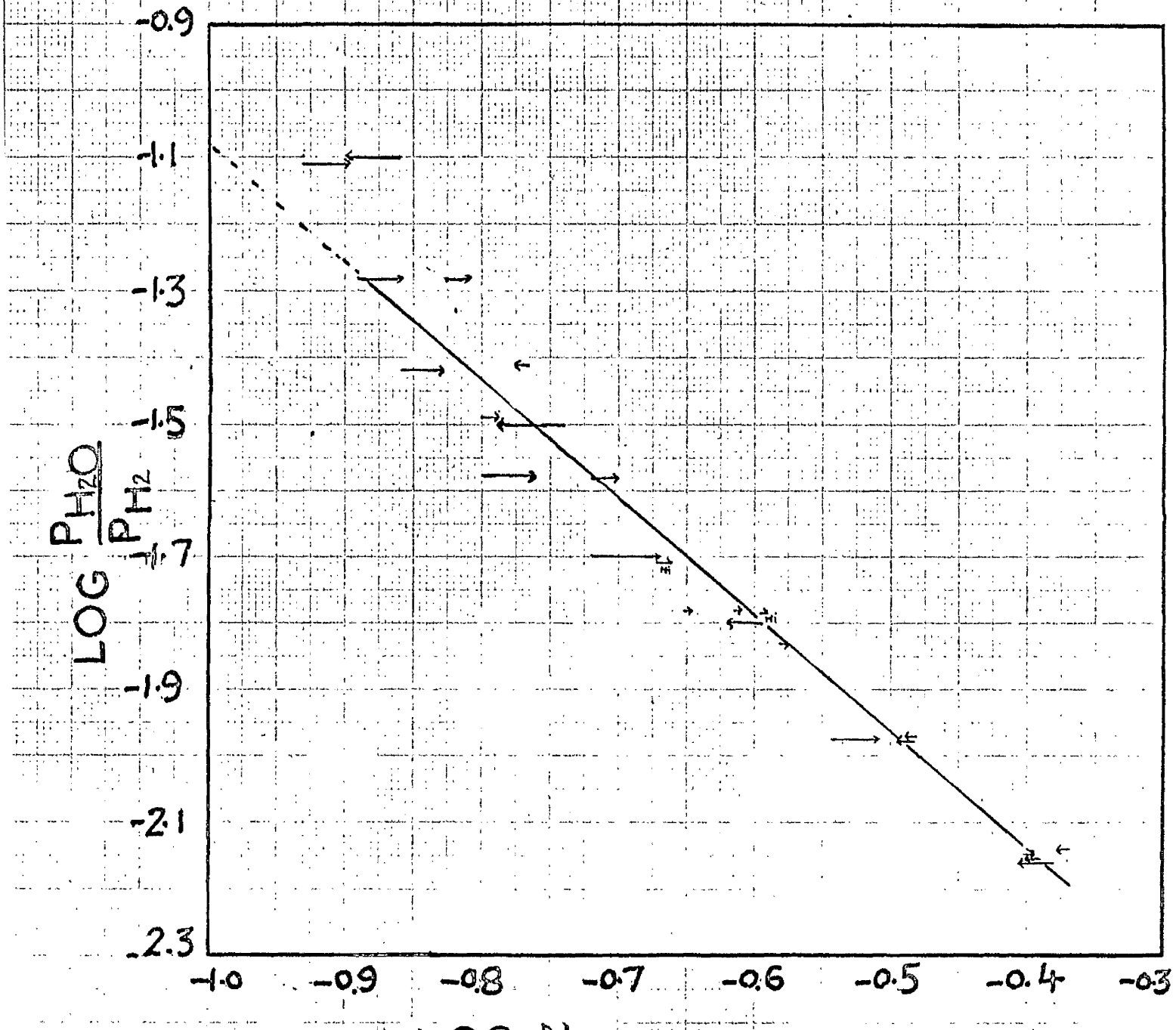


FIG 19 ESTIMATION OF THE LOG $\frac{P_{H_2O}}{P_{H_2}}$ LINE SHOWING RELEVANT EXPERIMENTAL DATA

the above expression for the equilibrium constant. Such a plot will only be possible if the condensed phases are of fixed composition. This in other words means that the chromic oxide which is in equilibrium with the vapour phase, i.e. hydrogen,- water vapour mixture should not change its composition with the chromium concentrations in the molten iron. Secondly, that the iron - chromium solutions should obey Raoult's Law. Both these assumptions were considered to be valid in some of the previous equilibrium studies of Cr - Cr_2O_3 - H_2O - H_2. If the condensed phases are of fixed composition, this problem can readily be handled in terms of equilibrium constant. But some of the recent investigations have reported:

(a) The existence of other oxides of chromium e.g. Cr_3O_4[30] and CrO[23, 29,] corresponding to varying chromium concentrations in the Fe - Cr - O system. This indicates that there is a gradual change in the composition of chromic oxide which is in equilibrium with chromium metal and hydrogen - water vapour mixture.

(b) That the iron chromium solutions may deviate quite considerably from Raoult's Law, both in the solid and liquid states as already discussed.[21 - 26]

Thus the change in the slope of the equilibrium plot log p_{H_2O}/p_{H_2} v log NCr is discussed in the light of each of these two possibilities.

Cr - O system involving an oxide of variable composition.

In fig. (19) is shown the relevant experimental data at 1700°C as log pH_2O/pH_2 v log NCr. Initial and final chromium contents are plotted to show the direction of movement. In drawing the most representative straight line through the experimental results, the direction of movement as well as the points nearer the pH_2O/pH_2 v NCr Fig (18) are considered more important. A line having a slope of -1.7 is the best fit for the experimental results indicating that the equilibrium data at 1700°C in the range 14 - 40% chromium is best served by considering the equilibrium between $Cr-Cr_{1.7}O - H_2O - H_2$, if the oxide is considered/contaning only Cr and oxygen and assuming solution/of Cr in Fe obey Raoult's Law. In this case the reaction and equilibrium constant could be considered,

$$Cr_{1.7}O + H_2 \rightleftharpoons H_2O + 1.7\ Cr$$

$$K = \frac{pH_2O}{pH_2} \cdot (a_{Cr})^{1.7}$$

$$K = \frac{pH_2O}{pH_2} \cdot (NCr)^{1.7}$$

"K" is calculated from the experimental data. Taking any point on the slop/in Fig (19) e.g.

$$\frac{pH_2O}{pH_2} = 0.0106$$

$N_{Cr} = 0.319$

$K = (0.0106) \times (0.319)^{1.7}$

$\log K = \log (0.0106) + 1.7 \log (0.319)$

$\log K = -2.828$

$K = 1.514 \times 10^{-3}$

Knowing the value of K, the free energy of formation of the reaction ($Cr_{1.7}O + H_2 \rightleftharpoons H_2O + 1.7\ Cr$) is calculated using the relation.

$$\Delta G = -RT \ln K$$

$$\Delta G = -4.575\ T \log K$$

$$\Delta G_{1700^oC} = -4.575 \times 1973 \times (-2.828)$$

$$\Delta G_{1700^oC} = 25,455 \text{ cals.}$$

From this the free energy formation of a mole of $Cr_{1.7}O$ is obtained by subtracting the free energy of formation of H_2O, as follows:

$$Cr_{1.7}O + H_2 \rightleftharpoons 1.7\ Cr + H_2O \qquad \Delta G_{1700^oC} = 25,455 \text{ cals.}$$

$$H_2 + \tfrac{1}{2} O_2 \rightleftharpoons H_2O \qquad \Delta G_{1700^oC} = -32,660 \text{ cals.}$$

$$1.7\ Cr + \tfrac{1}{2} O_2 \rightleftharpoons Cr_{1.7}O \qquad \Delta G_{1700^oC} = -58,115 \text{ cals.}$$

$$Cr_{1.7}O \qquad \Delta G_{1700^oC} = -58\ K \text{ cals.}$$

From the consistency of the present results, the equilibrium with chromous oxide may be considered possible. Chromous oxide has been said [35, 37, 38] to be stable at high temperatures and to disproportionate at lower temperatures to form chromic oxide, and chromium metal. Also from the previous investigations on Fe-Cr-O system, it has been suggested that there are numerous equilibria which may be considered.

For comparison the present results at 1700°C are further shown in Fig (20) along with the available data at 1600°C. The results are shown as log pH_2O/pH_2 v log NCr plot.

It can be seen from Fig. (20) that in the range 0 - 3% chromium, the results of Charlton[23], Chen & Chipman[20] and Lincsinski and Samarin[31] all show a slope of $-\frac{1}{2}$ indicating that in this range equilibrium with chromite is established and the following equilibrium reaction will determine the experimental conditions:

$$FeO.Cr_2O_3 + 4H_2 \rightleftharpoons 4H_2O + 2Cr + Fe$$

$$K = \left\{ \frac{pH_2O}{P_{H_2}} \right\}^4 \cdot (a_{Cr})^2$$

$$\log K = 4 \log \frac{pH_2O}{pH_2} + 2 \log a_{Cr}$$

$$\log \frac{pH_2O}{pH_2} \propto -\frac{1}{2} \log NCr$$

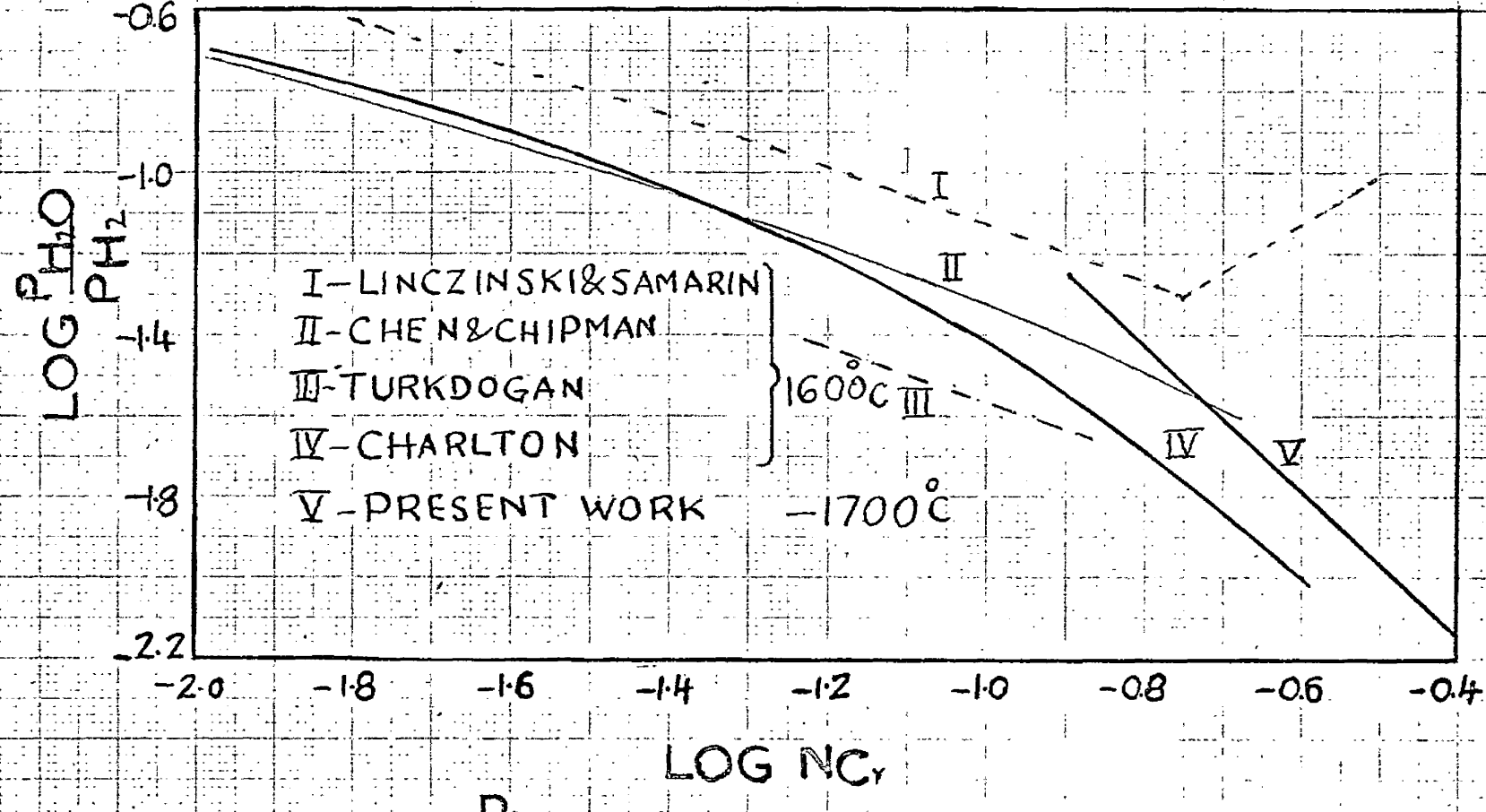


FIG 20 LOG $\frac{P_{H_2O}}{P_{H_2}}$ V LOG NC_r EQUILIBRIUM (1700°C)
& AVAILABLE DATA AT 1600°C

From 3 - 16% chromium, Lincsinski and Samarin[31] results show a slope of $\frac{-2}{3}$ indicating equilibrium with chromic oxide. Their results on the other hand give much higher values for equilibrium chromium concentrations as compared with the data of Chen & Chipman[20] and Charlton[23]. The reliability of Lincsinski and Samarin's[31] results is very much doubted. The experiments were carried out in alumina crucibles and the equilibrium was thought to have been attained as soon as an oxide layer appeared on top of the melt. This may not necessarily be true because it might have been necessary to oxidise considerable amounts of chromium before true equilibrium could be attained. Also the slope of their[31] curve is reversed beyond about 16% chromium, which is very confusing and opposite to what should be expected. Turkdogan's[32] data covers only a very restricted chromium range. His results in the range 6 - 12% chromium were represented by a line having a slope of $\frac{-2}{3}$ indicating that $Cr-Cr_2O_3$ equilibria will conform to the experimental conditions. His results give lower values for equilibrium chromium concentrations than those of other investigators[20, 23].

The slope of Chen & Chipman[20] curve in the range 3 - 10% chromium showed a continous change, indicating replacement of iron in chromite by chromium. Beyond 10% chromium the slope

of this curve[20] is approximately -1, thus corresponding to an oxide phase of the composition "CrO". In the original paper the slope of Chen and Chipman's[20] curve in the range 10 - 22% Cr was shown as $-\frac{2}{3}$. In fact this was an extrapolation from the lower results and the curve did not actually represent the experimental points. It may also be pointed out that Chen and Chipman[20] had only three experimental results in the range 10 - 22% Cr. Two of these did not show any change in chromium content during the experiments and thus they are doubted to be equilibrium values. Chen and Chipman's experiments lasted only for a maximum of 2 hrs. This might not be enough time at low oxygen pressures for a detectable movement for the attainment of equilibrium. The following equation shows an approximate change one could expect in two hours experiment using a gas mixture with a low partial pressure of oxygen. e.g.

Flow rate = 150 ml/min.

Let pH_2O = 20 m.m.

Duration of experiment = 2 hrs.

Atmospheric pressure = 760 m.m.

Total H_2O passed into the furnace will be

$$\frac{150 \times 120 \times 10}{760 \times 22400} \text{ g moles}$$

$$= \frac{180000}{760 \times 22400} \times 16 \times \frac{104}{48} \text{ g of Cr}$$

$$= 0.366 \text{ g chromium}$$

This shows a change of 1.25 wt% chromium in a 30 g charge. If for a given chromium content equilibrium $\frac{pH_2O}{pH_2}$ corresponds to $pH_2O = 9$ m.m. while that actually being used is 10 m.m. only, one tenth of the oxygen will be available for oxidation. Under these conditions only 0.125% Cr would be oxidised in a 2 hr. experiment.

Later when Chipman[29] reviewed this work[20] in the light of the investigation of Hilty, Forgeng and Feilman[30] on the oxide phases in Fe-Cr alloys, it was considered that the slope was steeper than $-\frac{2}{3}$ and it corresponds to a solid phase of composition Cr_3O_4. But it was further suggested that in the Cr_3O_4 range the data would be better served by a line of steeper slope e.g. one corresponding to CrO.

If the equilibrium established was that between chromous-oxide and chromium, then the following reaction

$$CrO + H_2 \rightleftharpoons H_2O + \underline{Cr}$$

and equation

$$K = \frac{pH_2O}{pH_2} \cdot a_{Cr}$$

will conform to the experimental conditions.

Charlton's[23] results in the range 3 - 7% chromium show a fairly rapid change in the slope which was explained as being due to a continous change in composition of the oxide phase in equilibrium with Fe-Cr-O system. From 7 - 10% chromium his[23] results show a slope of -1 and from 10 - 24% Cr to a slope of - 1.5. Charlton's original curve in the range 10 - 24% Cr corresponds to a slope of -1. This is based on few experimental points with distilled water in the saturators as a source of water vapour. But most of his experimental points in this range with lithium chloride solution as a source of water vapour are best served by a slope of -1.5. This is in very good agreement with the present work at 1700°C as evidenced from Fig.(20).

The free energy of formation of the oxide having a composition of $Cr_{1.5}O$ can be calculated from Charlton's[23] results (10 - 24%) at 1600°C as below.

$$Cr_{1.5}O + H_2 \rightleftharpoons H_2O + 1.5\ Cr$$

$$K = \frac{pH_2O}{pH_2} \cdot (N_{Cr})^{1.5}$$

$$\log K = \log \frac{pH_2O}{pH_2} + 1.5 \log N_{Cr}.$$

$$\log K = -2.9$$

$\Delta G = RT \ln K$

$= 4.575\ T \log K$

$= -4.575 \times 1673 \times -2.9$

$\Delta G_{1600^{\circ}C} = 24,851$ cals.

$\Delta G_{1600^{\circ}C}$ for the formation of a mole of $Cr_{1.5}O$ will be:

$Cr_{1.5}O + H_2 \rightleftharpoons 1.5\ Cr + H_2$ $\quad \Delta G_{1600^{\circ}C} = 24,851$ cals.

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ $\quad \Delta G_{1600^{\circ}C} = 34,060$ cals.

$1.5\ Cr + \frac{1}{2}O_2 \rightleftharpoons Cr_{1.5}O$ $\quad \Delta G_{1600^{\circ}C} = -58,911$ cals.

$Cr_{1.5}O$ $\quad \Delta G_{1600^{\circ}C} = -59$ K cals.

This calculation assumes that Fe-Cr solutions obey Raoult's Law. These suboxides of chromium representing equilibrium conditions in the present work and that of Charlton's [23] might possibly be in association with some iron, thus giving a composition of the type:

$$(Fe_x Cr_{n-x})_n O$$

Apart from the data of Chen & Chipman[20] and Charlton[23] at 1600°C and the present work at 1700°C there are numerous references (30, 35, 37, 38, 45) in the literature to the

existence of suboxides of chromium such as Cr_3O_4 and CrO. Hilty, Forgeng and Folkman[30] and Adachi and Iwamoto[66] in their studies of oxide inclusions in the cooled Fe-Cr alloys reported the presence of an oxide phase having a composition of Cr_3O_4 in equilibrium with the metal. Adachi & Iwamoto[66] have reported that chromium contents and oxygen potential had remarkable influence on the constitution of oxide inclusions.

This phase (Cr_3O_4) has the tendency to disproportionate below the liquidus as follows:-

$$3Cr_3O_4 \rightarrow 9Cr + 4Cr_2O_3$$

Kojima and Sano[45] have reported that chromium oxide behaved like chromous ion (CrO) in acidic slags when the chromium concentration in the equilibrium metal was higher than 3 pct. When the chromium range in the iron-chromium alloy was less than 3 pct, the oxidation-reduction reaction between chromium and iron in the two phases was represented by the following reaction:

$$4\,(FeO) + 3\,[Cr] \rightleftharpoons (Cr_3O_4) + 4\,[Fe]$$

Healy and Schottmiller[46] have reported a low melting liquid which they found could be produced by heating either an equimolar mixture of Cr_2O_3 and SiO_2 under an atmosphere of

hydrogen or heating a mixture of finely divided Cr_2O_3, Cr and SiO_2 held in tungsten crucible under purified argon in the temperature range of 1500 - 1600°C. The reaction product which could be quenched to a blue crystalline material was found to be chromous silicate "$Cr_2 SiO_4$". It is said to be unstable at room temperature, since on slow cooling it disproportionates in whole or in part to $Cr_2 O_3$, Cr and SiO_2 as follows:

$$3Cr_2SiO_4 \longrightarrow 2Cr_2O_3 + 2Cr + 2 SiO_2$$

No evidence of the existence of "CrO" as a pure substance was reported in the above investigation.

The lower oxide was obtained at normal temperature only in combination with silica. However, there has been no direct observation of these possible oxide phases and their existence has only been a matter of inference.

In the present work also, all the attempts to isolate the high temperature oxides of chromium failed. These oxides have been supposed to be stable only at high temperatures and if they exist will disproportionate with decrease in temperature as follows:

$$3CrO \rightleftharpoons Cr + Cr_2O_3$$

$$3 \quad (Fe_x Cr_{n-x})_n O \rightleftharpoons 3.x.Fe + (n-x) Cr_2O_3 + (n-x) Cr$$

To retain the oxide in its original phase, several rapid quenching techniques were tried without any success. These experiments to study the high temperature oxides of chromium were carried out by heating pellets of pure chromic oxide and pellets of a mixture of chromium metal and chromic oxide, corresponding to a composition of "CrO." The pellets were heated in molybdenum crucibles at 1700°C under different $\frac{H_2O}{H_2}$ ratios. These $\frac{H_2O}{H_2}$ ratios as given in Table (10) had low oxygen potentials.

TABLE (10)

Pellet No.		$\frac{pH_2O}{pH_2}$	Temperature °C	Duration of heating, Hrs.	Quenching technique.
1.	Cr_2O_3	0.007	1700	2	Furnace quenched
2.	Cr_2O_3 + Cr	"	"	"	"
3.	Cr_2O_3	0.02	"	"	"
4.	Cr_2O_3 + Cr	"	"	"	"
5.	Cr_2O_3	0.00365	"	"	"
6.	Cr_2O_3 + Cr	0.00365	"	"	"
7.	Cr_2O_3	0.00365	"	"	H_2O quenched.

All attempts to isolate "CrO" failed but some fusion of the mixtures was noticed. Microscopic examination of the polished quenched specimens and X-ray diffraction pictures

showed in all cases, the presence of metallic chromium and chromic oxide. Also there was no indication of any volatile oxide of chromium. Hydrogen passed over pure chromic oxide at 1950°C in a different set of experiments did not give any condensate in an experiment of 4 hr. duration.

Similar results have been reported by I.I.Olshanskii and Shlepov[67] in their study of the system $Cr-Cr_2O_3$

Their[67] experimental investigation on the system $Cr-Cr_2O_3$ started with the attempted synthesis of CrO. First they tried the possibility of forming CrO by the reduction of Cr_2O_3 with hydrogen. Experiments were carried out in a molybdenum furnace at 1470 - 1680°C for 15 - 180 mins. Microscopic investigation of the water quenched samplesshowed that in all the experiments, the reduction led to the formation of metallic chromium. But all these unsuccessful attempts to prepare solid chromous oxide could not settle the question of this phase under equilibrium conditions. They[67] found the eutectic temperature by studying the melting point of pellets of various compositions prepared from mixtures of Cr_2O_3 and metallic chromium and heated in argon. One eutectic point is reported to be at 1660°C and approximately 20% chromium. All other compositions are reported to have higher melting points.

Olshanski & Shlapov[67] checked the composition of eutectic melt fusions by heating in an argon atmosphere in metallic chromium crucibles at temperatures 20°C above the eutectic. They[67] cooled the crucibles in the furnace and analysed their contents by chemical and microscopic techniques. The compositions found in their experiments were reported to be close to the composition of eutectic mixture found in their preliminary experiments. The composition of eutectic liquid is reported to be very close to the gross composition of chromous oxide "CrO".

Olshanski and Shlapov[67] have constructed the phase diagram of the system Cr-Cr_2O_3 Fig (21), characterised by the considerable lowering of the melting point of chromium in the presence of 1% Cr_2O_3, a wide miscibility gap from (1-75% Cr_2O_3) in the liquid phase and the eutectic at 1660°C and 20% Cr.

From the binary Cr-Cr_2O_3 mentioned above Fig (21) it is seen that above the eutectic temperature of 1660°C, the $\frac{Cr}{O}$ ratio in the oxide phase increases with increasing temperature. The same trend is observed from the binary system Fe-Fe_2O_3 shown in Fig (1) where it is shown that above 1528°C the oxide phase in equilibrium with the metal will have a $\frac{Fe}{O}$ ratio more than 1.

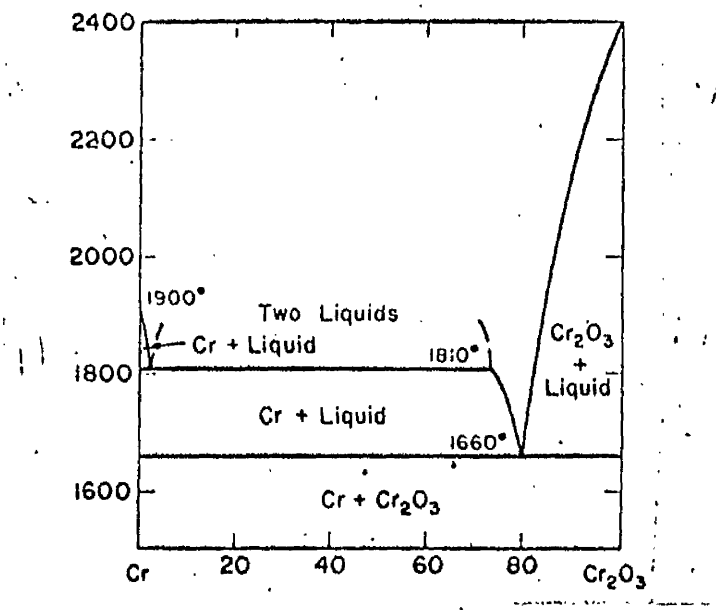


FIG21 THE CHROMIUM-OXYGEN PHASE DIAGRAM

From these two binaries ro $Cr-Cr_2O_3$ and $Fe-Fe_2O_3$, a possible ternary phase diagram can be constructed for Fe-Cr-O system at high temperatures. Such a tentative diagram is shown in Fig.(22) along with three binaries, $Fe-Fe_2O_3$, Fe-Cr, $Cr-Cr_2O_3$. The regions of different phases are shown in this ternary diagram as follows:

In the field AD, Fe-Cr, is a liquid metal solution of Fe-Cr-O alloy. In the phase field A,B,C,D, is the region of 2 liquids i.e. liquid metal and liquid oxide. The field C,D,E,F, consists of a liquid oxide phase. E.F. Fe_2O_3- Cr_2O_3 is the phase region comprising of solid oxide and liquid oxide.

This ternary diagram shows the general picture of metallic phases and oxide phases which are in equilibrium with each other, but the connodes are not known i.e. the exact chemical composition of the oxide in equilibrium with the metal is not known, but it is probably a Fe-Cr oxide. Assuming that the FeO-CrO liquid solution is ideal, the FeO concentrations can be calculated from the equilibrium equation as follows:

$$FeO + H_2 \rightleftharpoons H_2O + Fe \qquad \Delta G_{1700^\circ C} = 1,303 \text{ cals.}$$

$$\Delta G = Rt \ln K$$

$$\Delta G = -4.575\ T \log K$$

A	1528	0.16
C	1528	22.6
E	1583	28.3
B	1810	0.32
D	1810	23.0
F	1660	25.6

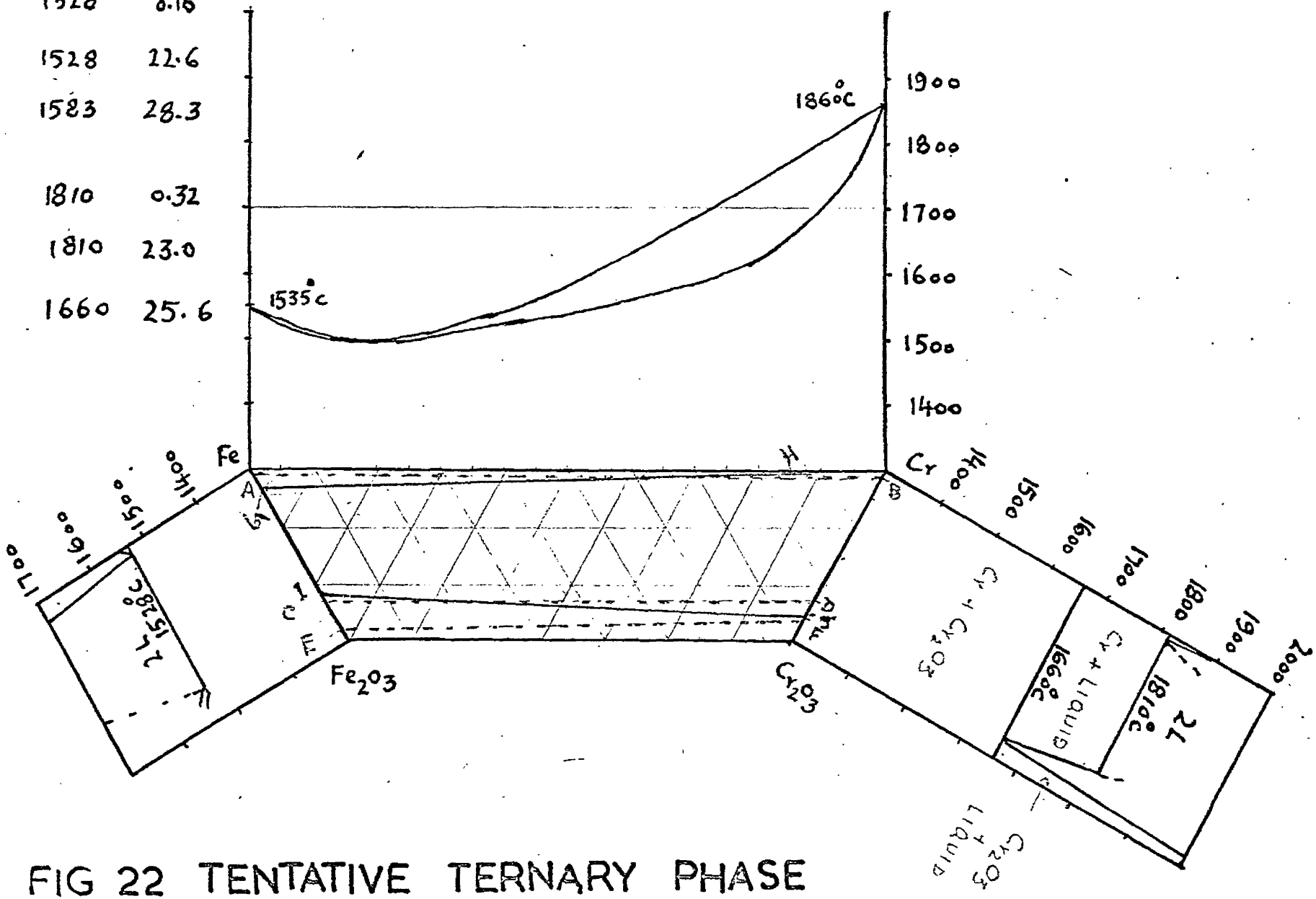


FIG 22 TENTATIVE TERNARY PHASE DIAGRAM FOR THE Fe–Cr–O SYSTEM

$$\Delta G = -\frac{1.303}{4.575 \times 1973} = -0.144$$

$$\log K = -0.144$$

$$K = 0.718$$

$$K = \frac{pH_2O}{pH_2} \cdot \frac{aFe}{aFeO}$$

$$K = \frac{pH_2O}{pH_2} = \frac{NFe}{NFeO}$$

$$NFeO = \frac{pH_2O}{pH_2} \cdot \frac{NFe}{K}$$

Using this relation, NFeO corresponding to various Cr concentrations and $\frac{pH_2O}{pH_2}$ at 1700°C (from Fig (18) were calculated. These values are given in Table (11).

TABLE (11)

No.	NCr	NFe	$\frac{pH_2O}{pH_2}$	NFeO
1.	0.168	0.832	0.035	0.04
2.	0.199	0.801	0.025	0.02
3.	0.245	0.755	0.017	0.013
4.	0.319	0.681	0.01	0.0095
5.	0.4	0.6	0.0075	0.0063

These results are shown graphically in Fig.(23)

At 1700°C, the composition of the metal (Fe-Cr-O) will lie on the line GH and that of the liquid oxide on the line IJ in Fig. (22). Under similar conditions the position of these lines will be slightly different at 1600°C. For each Cr concentrations in the metal there will be a unique equilibrium composition of oxide phase and oxygen potential for a given temperature. This suggests that equilibrium is not established with Cr_2O_3 but with a liquid iron-chromium oxide. The equilibrium could be represented as follows:-

$$(Fe_x\ Cr_{n-x})_nO + H_2 \rightleftharpoons H_2O + n \cdot x \cdot Fe + (n-x)\ Cr$$

$$K = \frac{pH_2O}{pH_2} \cdot \frac{(a_{Cr})^{(n-x)} \cdot (a_{Fe})^{(x)}}{(Fe_xCr_{n-x})_nO}$$

The oxide $(Fe_xCr_{n-x})_nO$ will have a variable composition in which the ratio of $\frac{Cr}{Fe}$ will increase with increasing chromium concentrations in the metal and with decreasing oxygen potential.

Assuming the liquid oxide to be a solution of ferrous oxide and chromous oxide (both oxides will probably be non stoichiometric) then the equilibrium could be written:

$$FeO + H_2 \rightleftharpoons Fe + H_2O$$

$$CrO + H_2 \rightleftharpoons Cr + H_2O$$

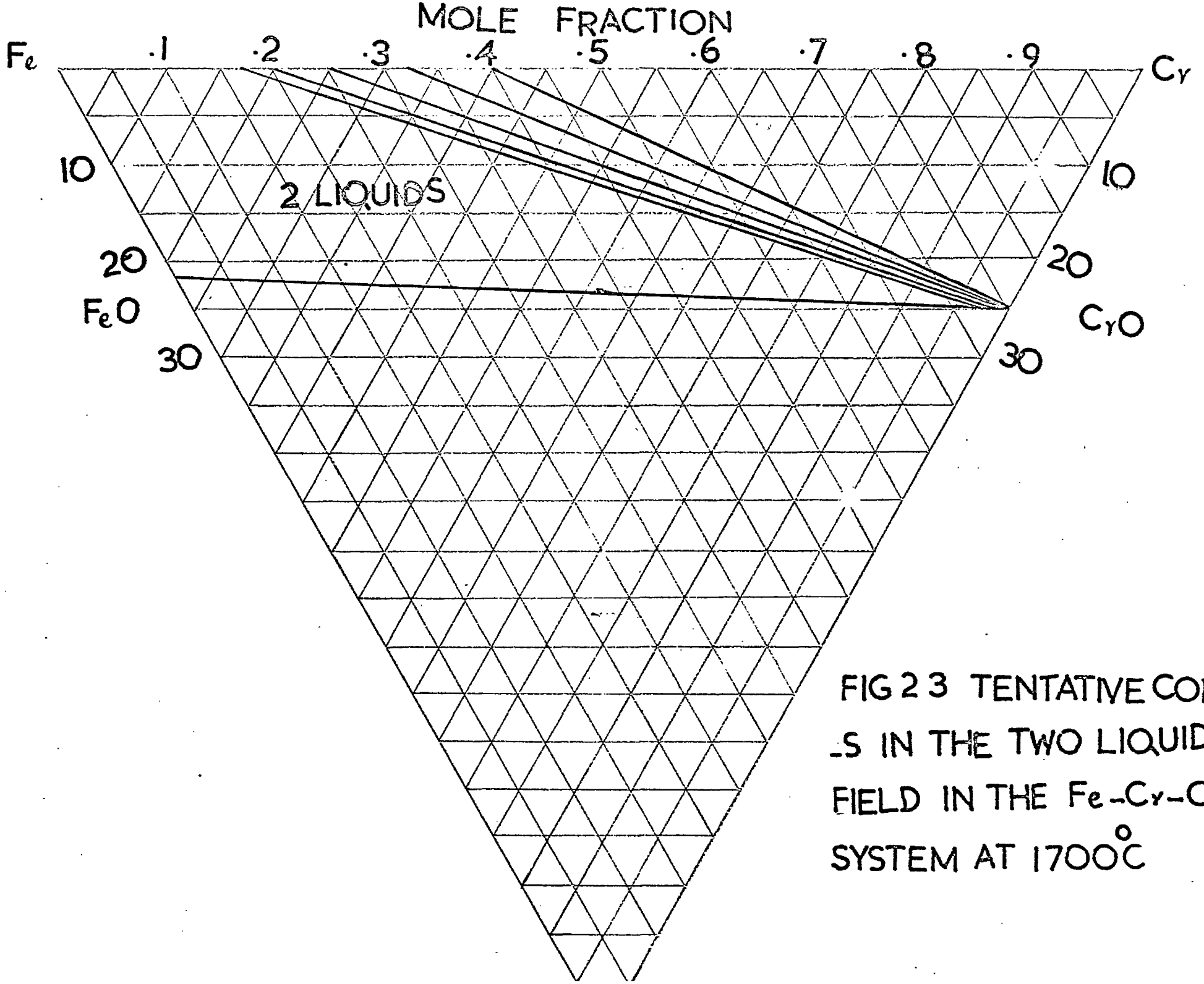


FIG 2 3 TENTATIVE CONNODE
_S IN THE TWO LIQUID
FIELD IN THE Fe-Cr-O
SYSTEM AT 1700°C

for which

$$K = \frac{pH_2O}{pH_2} \cdot \frac{a_{Fe}}{a_{FeO}}$$

$$K = \frac{pH_2O}{pH_2} \cdot \frac{a_{Cr}}{a_{CrO}}$$

calculations based on the first reaction would indicate a low activity of ferrous oxide in the oxide phase. For an alloy of 15.76% Cr the NFeO in the equilibrium oxide phase would be about 0.04 while in one containing 30.28% Cr it would be about 0.0095 at 1700°C.

From the calculations based on the oxide as an ideal solution, the Cr/Fe ratio in the oxide would be high. As a first approximation at higher Cr contents it would be considered as almost entirely chromium oxide. Assuming from the data of Olshanski and Shlepov[67] that the equilibrium composition of the oxide is approximately "CrO" at 1700°C, the free energy of formation of the oxide can be calculated from the equilibrium,

$$CrO + H_2 \rightleftharpoons H_2O + Cr$$

$$K = \frac{pH_2O}{pH_2} \cdot a_{Cr}$$

$$= \frac{pH_2O}{pH_2} \cdot N_{Cr}$$

$$\log K = \log \frac{pH_2O}{pH_2} + \log NCr$$

Taking a point on the line in Fig (19).

$$\log K = +1.52 + (-0.75)$$

$$\log K = -2.27$$

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ_{1700^\circ C} = -4.575 \times 1973 \times (-2.27)$$

$$\Delta G^\circ_{1700^\circ C} = 20{,}490 \text{ cals.}$$

$CrO + H_2 \rightleftharpoons H_2O + Cr$	ΔG_{1700}	= 20,490 cals.
$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$	ΔG_{1700}	= -32,697 cals.
$Cr + \frac{1}{2}O_2 \rightleftharpoons CrO$	$\Delta G_{1700^\circ C}$	= -53,187 cals.
		= -53 k cals.

Calculation yields a free energy of formation at $1700^\circ C$ of 53 K cals. This calculation is based on Fe-Cr alloys at $1700^\circ C$ obeying Raoult's Law. The data in Fig. (19) where the gradient of the log $\frac{pH_2O}{pH_2}$ v log NCr plot is less than minus one, suggests that if the oxide composition is approximately "CrO" then there would be a positive deviation from ideality in the liquid Fe-Cr system.

No thermal data is available on the free energy of formation of "CrO" but some idea of a possible value might be deduced from other data. There is thermodynamic data for CrF_2, $CrCl_2$ and $CrBr_2$ where Cr has the same valency as in CrO. In the periodic table horizontal relationship exists between the elements Ti, V, Cr, Mn, Fe, Cd and Ni. In addition to the vertical similarities, it is found that horizontal similarities exist for certain group of elements. This is particularly pronounced for the Lanthanide elements but it is also quite important in the transition elements. The elements in the transition class show striking resemblence to each other, particularly in their physical properties. The oxidation states are very numerous and compounds are highly coloured.

Plots of heats of formation ($\Delta H_{298^\circ K}$) and free energies of formation (ΔG) for the halides and oxides of the transition metals, Ti, V, Cr, Mn, Fe, Co and Ni, are shown in Fig (24) and Fig (25) respectively as a function of their atomic numbers. The ΔG for the oxides are plotted at $1973^\circ K$ ($1700^\circ C$), for the fluorides at $1500^\circ K$ and for the chlorides and bromides at $1000^\circ K$. These plots show that the Mn compounds are the odd ones in these series while the chromium halides fit into the general pattern. All the metals except Cr have data for oxides in which

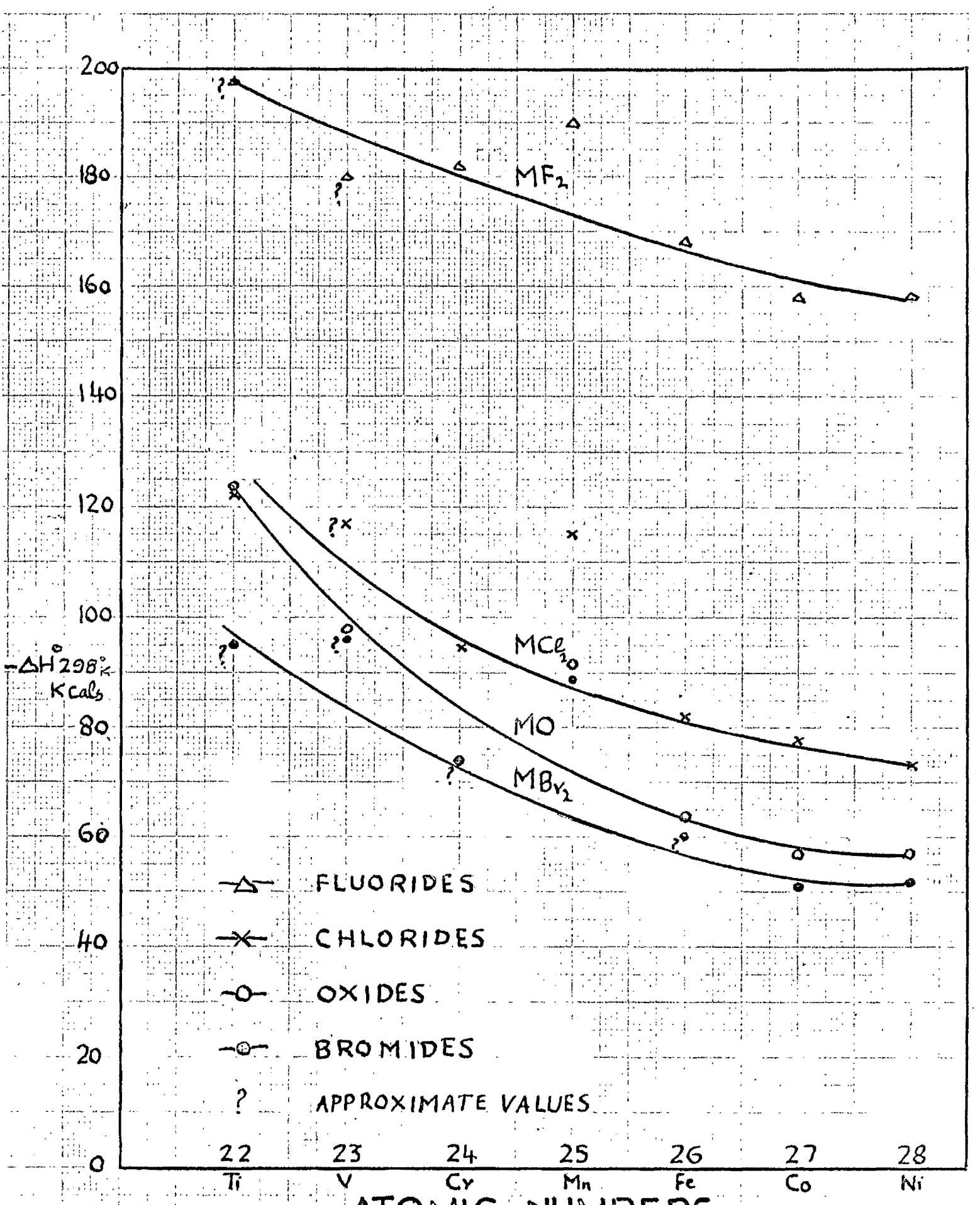


FIG 24 HEATS OF FORMATION OF DIVALENT-HALIDES & DIVALENT OXIDES

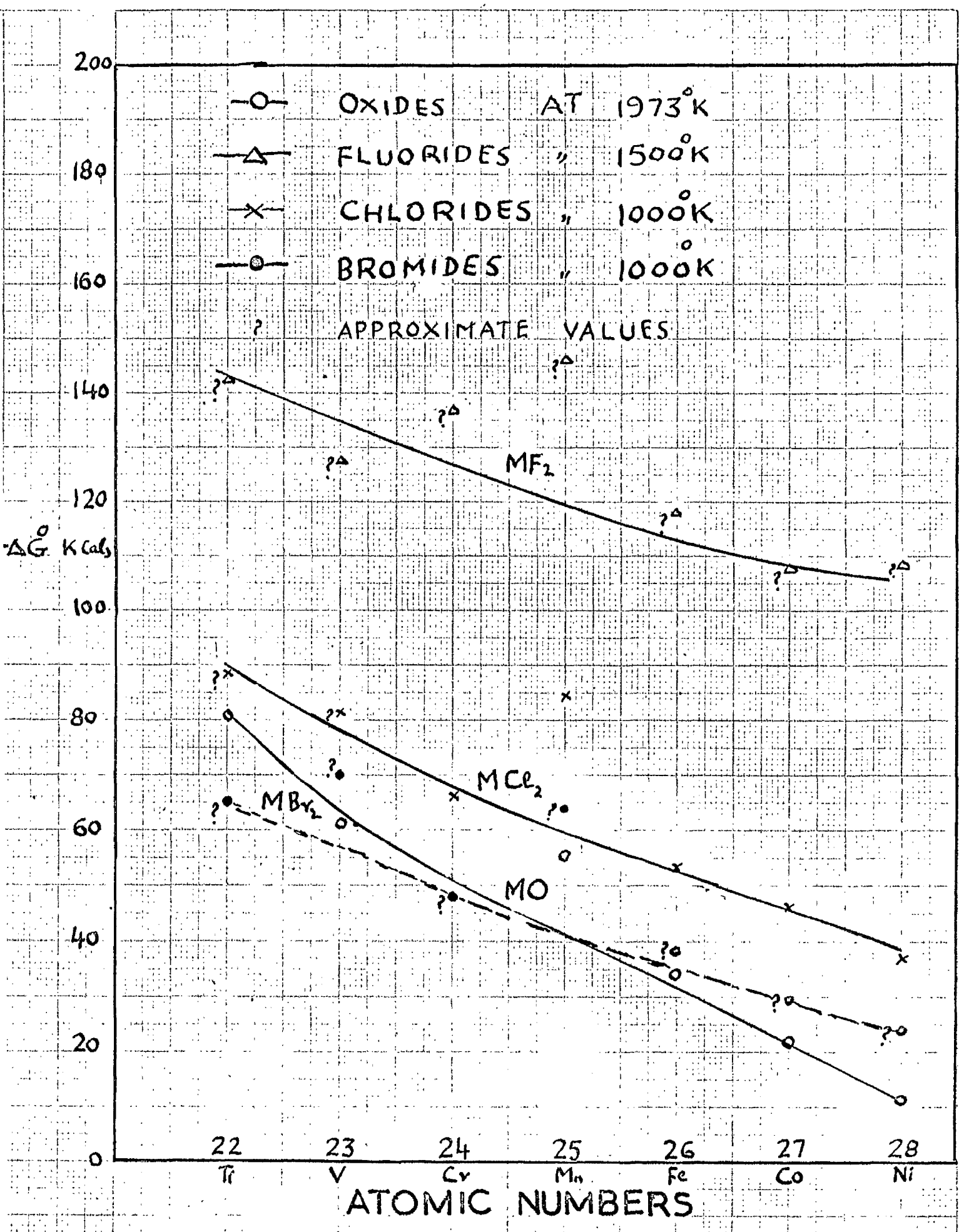


FIG 25 FREE ENERGIES OF FORMATION OF DIVALENT HALIDES & DIVALENT OXIDES

the metal is divalent. Some of which are only stable at elevated temperatures. If the chemical relationship holds one might expect chromium to have a lower oxide "CrO", and from Figs (24) and (25), the $\Delta H_{298^{\circ}K}$ and $\Delta G_{1973^{\circ}K}$ would be approximately -84k cals and -52k cals. The value of $\Delta G_{1973^{\circ}K}$ = -53 k cals for CrO, calculated from the present results.

This survey of the experimental data on the iron-chromium oxygen equilibrium leads to the conclusion that the oxide phase in equilibrium with the liquid alloys is not Cr_2O_3 but a lower oxide of chromium with an approximate composition (Fe Cr)O. The ratio of $\frac{Cr}{Fe}$ depends on the composition of the alloy but will be predominantly Cr and for the alloys studied in the present investigation it can be assumed to be almost entirely a chromium oxide. The free energy of formation of the oxide is of the order of 50 to 55 k cals. The data suggest that there is a positive deviation from ideality in the liquid Fe-Cr alloys but the magnitude of the deviation cannot be calculated unless reliable data for the free energy of formation of the oxide was available.

iii) APPLICATION OF RESULTS TO THE DECARBURISATION OF CHROMIUM STEELS.

When decarburizing chromium steels a practical knowledge of the equilibrium carbon contents corresponding to any particular chromium concentrations is essential to minimise the chromium losses to the slag. Dennis & Richardson(36) have found the relation between carbon contents and $\frac{p^2CO}{pCO_2}$ ratios in Fe-Cr alloys at 3 different chromium concentrations and at temperatures of 1560, 1660 and 1760°C. From these values the equilibrium relation between C contents and $\frac{p^2CO}{pCO_2}$ has been estimated at 1600°C and 1700°C at different chromium contents. This is shown in Fig (26.)

From the present results at 1700°C and from Charlton's(23) results at 1600°C, $\frac{p^2CO}{pCO_2}$ ratios were calculated at 5 different chromium concentrations as follows.

Knowing the standard free energy of formation for the reaction:

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O$$

which is $\Delta G_{1700^oC} = -52,697$ cals (Elliot & Gleiser)

$$K = \frac{pH_2O}{pH_2 p^{\frac{1}{2}}O_2}$$

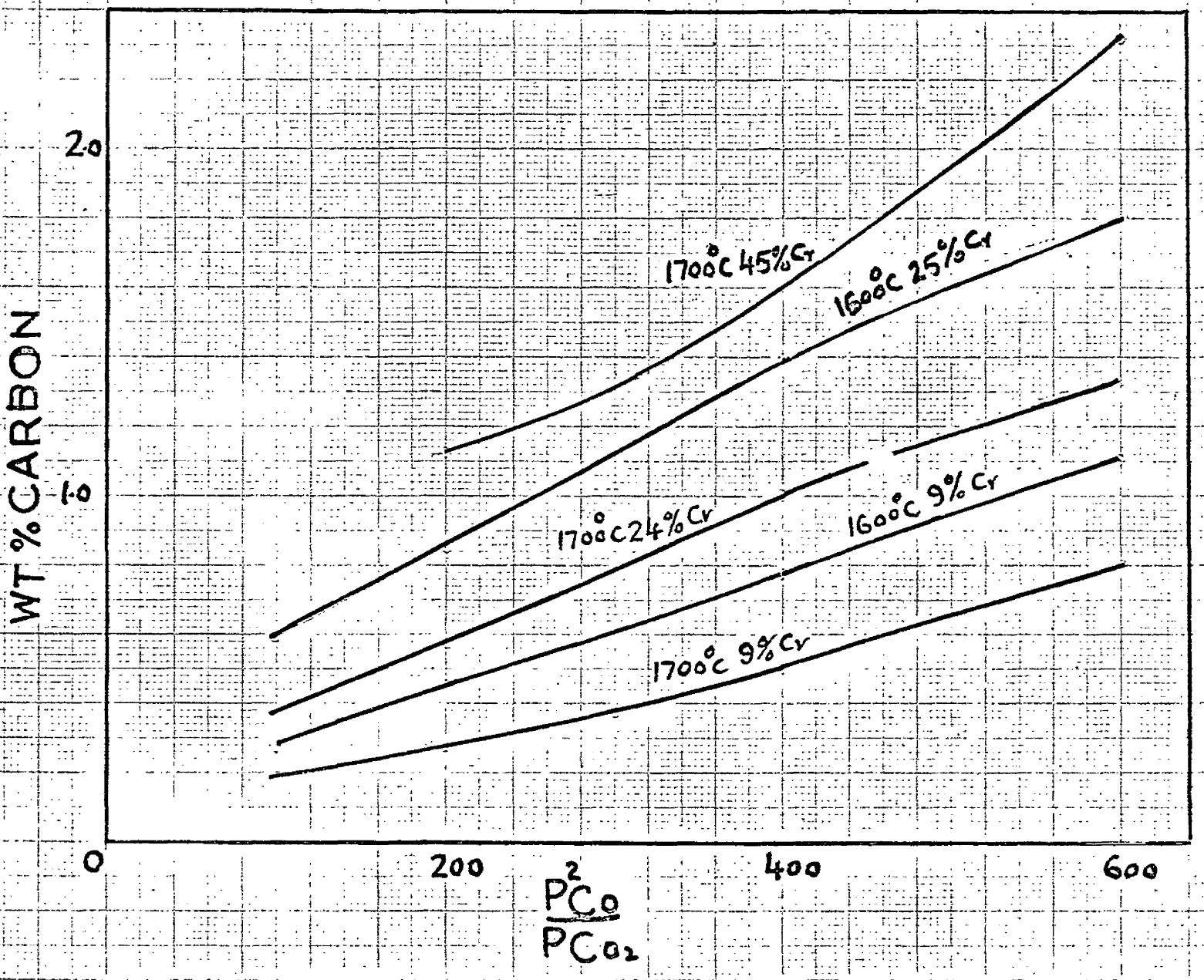


FIG 26 EXTRAPOLATED VALUES FROM DENNIS & RICHARDSON'S DATA.

is calculated.

$$\Delta G^{0} = -RT \ln K$$

$$= 4.575 \times 1973 \times \log K$$

$$\log K = \frac{-\Delta G}{4.575 \times 1973} = \frac{32.697}{9026.475}$$

$$\log K = 3.62$$

$$K = 4.169 \times 10^{3}$$

Then from the present results at 1700°C taking any point from the plot pH_2O/pH_2 v NOr Fig (18) e.g.

$$\frac{pH_2O}{pH_2} = 0.035$$

Cr = 15.76% NOr = 0.168

The partial pressure of oxygen in equilibrium with the above pH_2O/pH_2 and Cr concentrations was calculated from the equilibrium equation:

$$K = \frac{pH_2O}{pH_2 \cdot p\,O_2^{\frac{1}{2}}}$$

$$p^{\frac{1}{2}}O_2 = \frac{pH_2O}{pH_2} \cdot \frac{1}{K}$$

$$= 0.035 \times \frac{1}{4.169 \times 10^{3}}$$

$$= 8.39 \times 10^{-6}$$

Also from the standard free energy of formation for the reaction:

$$CO + \tfrac{1}{2}O_2 \rightleftharpoons CO_2$$

$$\Delta G_{1700^oC} = -26,741 \text{ cals (Elliot \& Gleiser)}$$

$$K = \frac{pCO_2}{pCO \cdot p^{\frac{1}{2}}O_2}$$

K can be calculated

$$\Delta G = -RT\ln K$$

$$= -4.575 \times 1973 \log K$$

$$\log K = -\frac{\Delta G}{4.575 \times 1973} = \frac{26,743}{9026.475}$$

$$\log K = 2.96$$

$$K = 9.12 \times 10^2$$

Thus knowing the values of K and $p^{\frac{1}{2}}O_2$, the ratio pCO_2/pCO is calculated from the equilibrium equation:

$$K = \frac{pCO_2}{pCO \cdot p^{\frac{1}{2}}O_2}$$

$$\frac{pCO_2}{pCO} = K \cdot p^{\frac{1}{2}}O_2$$

$$= 9.12 \times 10^2 \times 8.39 \times 10^{-6}$$

$$\frac{pCO_2}{pCO} = 7.65 \times 10^{-3}$$

As the partial pressure of $p^{\frac{1}{2}}O_2$ is very small, therefore:

$$pCO_2 + pCO \doteq 1 \text{ atm.}$$

$$pCO = 1 - pCO_2$$

$$\frac{pCO_2}{pCO} = 7.65 \times 10^{-3}$$

$$pCO_2 = (7.65 \times 10^{-3}) \times pCO$$

$$= (7.65 \times 10^{-3}) \times (1 - pCO_2)$$

$$= 7.65 \times 10^{-3} - 7.65 \times 10^{-3} \times pCO_2$$

$$pCO_2 + 7.65 \times 10^{-3} \times pCO_2 = 7.65 \times 10^{-3}$$

$$pCO_2 (1 + 7.65 \times 10^{-3}) = 7.65 \times 10^{-3}$$

$$pCO_2 = \frac{7.65 \times 10^{-3}}{1 + 7.65 \times 10^{-3}}$$

This given a very small value of pCO_2 and therefore in the above equilibrium reaction CO pressure can be taken as approximately 1 atm.

Thus $pCO_2 = 7.65 \times 10^{-3}$

$pCO = 1$

Knowing the values of pCO_2 and pCO, the ratio $\frac{p^2CO}{pCO_2}$ can be calculated:

$$\frac{p^2CO}{pCO_2} = \frac{1}{7.65 \times 10^{-3}}$$

$$\frac{p^2CO}{pCO_2} = 130.7$$

Also the activity of C can be calculated from the reaction:

$$C + CO_2 \rightleftharpoons 2\,CO$$

$\Delta G_{1700^oC} = -26,679$ cals (Elliot & Glaiser)

$$\Delta G = -RT \ln K$$

$$\log K = \frac{-\Delta G}{4.57 \times 1973}$$

$$= \frac{26,679}{9026.479}$$

$$\log K = 2.96$$

$$K = 9.12 \times 10^2$$

$$K = \frac{p^2CO}{pCO_2 * a_C}$$

$$9.12 \times 10^2 = \frac{1}{7.65 \times 10^{-3}} * \frac{1}{a_C}$$

$$a_C = \frac{1}{7.65 \times 10^{-3}} * \frac{1}{9.12 \times 10^2} = \frac{1}{6.98}$$

$$a_C = 0.14$$

Similarly from Charlton's[23] results at 1600°C p^2CO/pCO_2 and a_C were calculated form different chromium concentrations. Then by interpolation to the required chromium

concentrations at 1700°C and 1600°C from Fig (26), the C concentrations which are in equilibrium with particular p^2CO/pCO_2 ratios were calculated. These values which were calculated from the present results at 1700°C and Charlton's[23] data at 1600°C are given in Table 12.

TABLE 12.

Temperature °C	Cr wt%	$\frac{(pCO)^2}{pCO_2}$	C wt%	eC
1600	9.57	102	0.3	0.17
"	13.45	145	0.475	0.26
"	16.97	233	0.7	0.4
"	20.32	322	1.0	0.56
"	25.8	418	1.35	0.73
1700	15.76	130	0.3	0.14
"	18.72	183	0.43	0.20
"	23.16	269	0.7	0.29
"	30.28	456	1.3	0.50
"	38.26	610	2.025	0.67

In Fig (27) carbon contents are shown as the function of the chromium content at 1600°C and 1700°C. The curve shown for 1000°C has been extrapolated from the results at 1600°C and 1700°C, on the basis of a straight line for the log MCr/eC v $\frac{1}{T°K}$ plot.

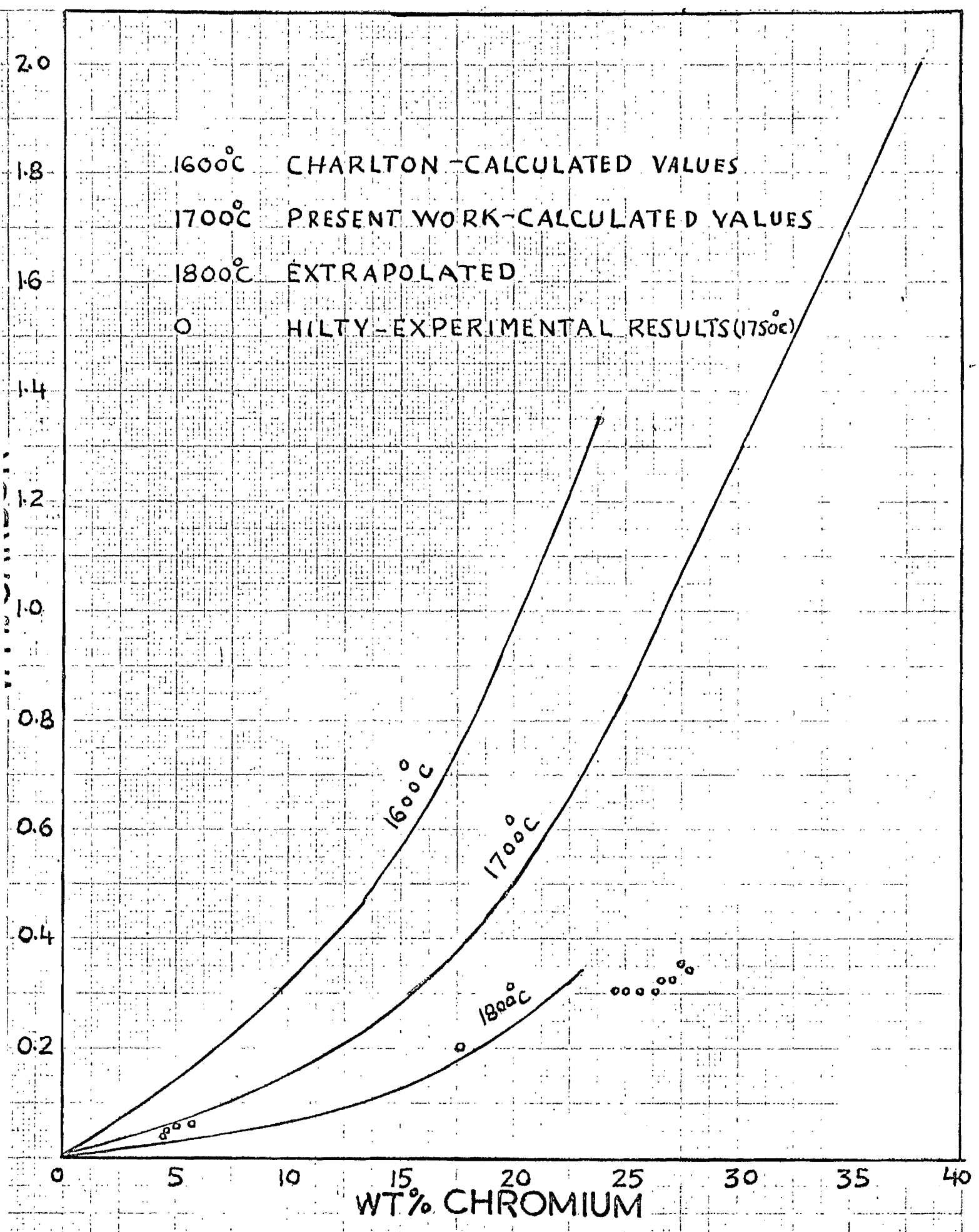


FIG 27 EQUILIBRIUM BETWEEN CARBON & CHROMIUM IN LIQUID IRON

Hilty's[35] experimental points at 1750°C are also shown in this diagram. The extent to which the calculated curves depart from Hilty's[35] experimental results could be attributed to many extrapolations and interpolations and also due to accumulated errors from all the separate investigations involved in the comparison.

Fig (27) shows the chromium and carbon concentrations controlled by the equilibrium of the equation:

$$CrO + C \rightleftharpoons Cr + CO$$

This decarburisation equilibrium is suggested from the experimental results in the present work at 1700°C and that of Charlton's[23] data at 1600°C.

The curves of Fig (27) indicate the minimum carbon content at any temperature which can be achieved by oxidation of the melt without also oxidising the chromium. High temperatures and low chromium initial charges are thus very desirable for the production of chromium steel of exceptionally low carbon content.

A C K N O W L E D G E M E N T S

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